Development of a new method for aggregate quality control in civil engineering applications

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Erklärung

Hiermit erkläre ich die vorliegende Dissertation eigenständig und ohne unerlaubte Hilfe verfasst habe. Er wurden ausschließlich die in der Arbeit angegebenen Quellen und Hilfsmittel benutzt.

Clausthal-Zellerfeld, 15.10.2015

Alireza Tayebi

Alireza Tayebi

To the people of the world

The only source of knowledge is experience.

[Albert Einstein]

Have patience. All things are difficult before they become easy.

[Sa´adi]

Abstract

Civil engineering has fulfilled many different needs of human life. It has provided much ease, comfort, and pleasantness to daily life through such conveniences as the construction of homes, buildings, skyscrapers, railways, subways, roads, and tunnels. Each of these applications of civil engineering would not be possible without the use of natural crushed stone. In fact, natural crushed stone and aggregates are the building block of all of the aforementioned constructions. As a result, worldwide production and consumption of aggregates is steadily increasing. Due to a limited quantity of natural resources and the millions of years needed for their renewal, quality management of raw materials is key to sustainable development and continued success. Hand in hand, sustainable development policies are imperative to the optimal usage of the reserves.

Quality control and quality assurance are the two main elements of quality management. Different methods and procedures have been proposed in order to maintain consistent quality of the aggregates, as the principal constituent of various forms of civil engineering constructions. Railroad construction and asphalt production are two key usages of aggregates. The quality of the aggregates in the aforementioned applications plays a significant role in life span of the product. High quality aggregate, while more costly at the beginning, increases the life cycle and life cycle value, decreases life cycle costs, and in turn leads to improved public service quality, a substantial parameter of sustainable policy.

The disintegration and breakdown of aggregates over time has been the subject of many bodies of research throughout the years, resulting in the publication of various procedures and methods to be utilized in determining hard rock quality and durability. However, the proposed previous methods are time-consuming, non-reproducible, and non-representative. Therefore, they are not able to recognize the quality of aggregates in a correct manner. Use of aggregates with lack of sufficient quality results in their physical, chemical, and mechanical failure. The aggregate quality issue becomes more critical when it comes to the usage of aggregates for railway-ballast/asphalt production. In the first part of this study, two parameters were developed for the purpose of quality assurance and quality control of aggregate for railway ballast applications. Based on the results of thousands of field and laboratory experiments, these two parameters, loss on ignition (LOI) and magnetic susceptibility (MAG), can identify the quality of aggregate prior to its exploitation and production. LOI and MAG were implemented in three igneous hard rock quarries and have shown to provide accurate results in a more effective and efficient manner.

The stripping of asphalt, which is a problem often confronted with the asphalt industry, is another important topic discussed in this thesis. Shortly after initial construction, many asphalt roads need to be re-asphalted, frequently due to a loss of adhesion between the aggregate surface and the bitumen layer. In order to eliminate this phenomenon, different mechanisms and theories have been presented over the past century, though the problem has never been truly clarified nor solved.

The stripping of asphalt has its consequences: loss of stability and swelling of the asphalt. The second part of this study discusses the problem of asphalt affinity. More than 1,300 asphalt samples were prepared and tested in order to identify and recognize the main problem and consequently develop appropriate preventative strategies to improve the quality of asphalt concrete for use in roads. With regard to this issue a new concept, the Water Discharge Theory, is presented. This theory explains that the loss in affinity between aggregate surface and bitumen layer is a function of aggregate´s inherent water content. With a basis in this theory, the impact of LOI and MAG values of asphalt aggregates on the quality of the asphalt were studied. According to our obtained results the direct effects of LOI and MAG (values of aggregates) on stripping and consequently on quality of asphalt were confirmed.

With regard to this issue, the main problem is that in most quarries, the mining techniques are not based on any engineering classification of rocks and as a result, selective quarrying methods are not applied. In fact, since most of the quarrying approaches are not selective, therefore normally high and poor quality rocks are blasted and mixed together in a muck-pile and consequently are also crushed together. This procedure ends up to the production of aggregates with unknown quality aspects, which can bring forth unexpected unwanted results in their further usages.

Online recognition of aggregate quality for railway ballasts and asphalt applications was achieved through the development of the two new parameters, LOI and MAG. These parameters proved successful in three different quarries. Based on the application purposes, threshold values for each parameter were also determined.

Zusammenfassung

Das Bauingenieurwesen erfüllt die unterschiedlichsten Anforderungen des menschlichen Lebens. Viele Vorteile und Annehmlichkeiten im täglichen Leben wie Häuser, Hochhäuser, Eisenbahnen, U-Bahnen, Straßen und Tunnel wären ohne dieses undenkbar. Diese Ingenieurleistungen wären jedoch ohne die Verwendung von gebrochenem Naturstein nicht möglich, da diese eine wichtige Grundlage der oben genannten Bauwerke sind. Als Folge dessen steigen die weltweite Produktion und der Verbrauch von Gesteinskörnungen stetig an. Auf Grund der begrenzten Menge an natürlichen Ressourcen und der Jahrmillionen die deren Erneuerung bedarf, ist ein Qualitätsmanagement für die Rohstoffe der Schlüssel für eine nachhaltige Entwicklung und einen stetigen Erfolg. Einhergehend mit einer Methode zur nachhaltigen Gewinnung ist die optimale Ausnutzung der Reserven erforderlich.

Qualitätskontrolle und Qualitätssicherung sind die zwei Hauptelemente des Qualitätsmanagements. Verschiedene Methoden und Verfahren werden empfohlen, um eine gleichbleibende Qualität der Gesteinskörnungen zu gewährleisten. Gesteinskörnungen werden zum Beispiel als Gleisschotter und zur Asphaltproduktion eingesetzt. Die Qualität der Gesteinskörnungen ist entscheidend für die Lebensdauer dieser Produkte. Gesteinskörnungen mit hoher Qualität mögen zu Beginn kostenintensiver sein, haben dafür aber eine längere Lebensdauer und verursachen geringere Unterhaltungskosten.

Der Zerfall von Gesteinskörnungen war Gegenstand vieler wissenschaftlicher Untersuchungen in den letzten Jahrzehnten. Daraus resultierten Veröffentlichungen sowie verschiedene Verfahren und Methoden, um die Qualität und Haltbarkeit von Festgesteinen zu bestimmen. Die bisherigen Methoden sind jedoch zeitintensiv, nicht reproduzierbar und nicht repräsentativ. Deswegen ist es nicht möglich, mit diesen Methoden die Gesteinsqualität in erforderlicher Weise zu ermitteln. Die Verwendung von Gesteinskörnungen mit geringer Qualität führt zu physikalischen, chemischen und mechanischen Problemen. Das Thema der Qualität von Gesteinskörnungen ist von besonderer Bedeutung, wenn diese als Gleisschotter oder zur Herstellung von Asphalt verwendet werden. Im ersten Teil der vorliegenden Arbeit werden zwei Parameter entwickelt, die zur Bestimmung und Kontrolle der Qualität von Gesteinskörnungen dienen, die als Gleisschotter verwendet werden. Basierend auf den Ergebnissen von tausenden Feld- und Laboruntersuchungen konnten zwei Parameter, Glühverlust (LOI) und magnetische Suszeptibilität (MAG), identifiziert werden, mit deren Hilfe die Qualität von Gesteinskörnungen vor der Gewinnung und Aufbereitung bestimmt werden kann. Die Parameter LOI und MAG wurden in drei verschiedenen magmatischen Steinbrüchen zur Bestimmung der Gesteinsqualität verwendet und lieferten effektiv und effizient zuverlässige Ergebnisse.

„Stripping", das ein großes Problem für die Asphaltindustrie darstellt, ist das zweite wichtige Thema diese Arbeit. Kurz nach dem Einbau müssen viele Asphaltdecken erneuert werden, weil die Haftung zwischen der Oberfläche der Gesteinskörnungen und dem Bitumen verloren geht. Bei dem Versuch dieses Problem zu lösen, sind im letzten

Jahrhundert viele Verfahren und Theorien entwickelt worden. Dennoch konnte das Problem nie gelöst werden.

Stabilitätsverlust und Quellung sind die Konsequenzen des „Strippings“. Im zweiten Teil der vorliegenden Arbeit wird das Problem fehlender Affinität zwischen Gesteinskörnungen und Bitumen im Asphalt untersucht. Mehr als 1.300 Asphaltprobenkörper wurden hergestellt und untersucht, um das Hauptproblem zu identifizieren und zu bestimmen. Daraus resultierend wurde eine zielgerichtete präventive Strategie entwickelt, um die Qualität des Asphalts zu verbessern. In Bezug auf dieses Thema wird ein neues Konzept präsentiert: Water Discharge Theory. Diese Theorie besagt, dass der Verlust der Affinität zwischen der Oberfläche der Gesteinskörnungen und dem Bitumen eine Funktion des Wassergehalts der Gesteinskörnungen ist. Basierend auf dieser Theorie wurde der Einfluss von LOI und MAG der zur Herstellung des Asphalts verwendeten Gesteinskörnungen auf die Asphaltqualität untersucht. Anhand der erhaltenden Resultate konnte der direkte Einfluss von LOI- und MAG-Werten der Gesteinskörnungen auf das „Stripping“ und demzufolge auch auf die Asphaltqualität bestimmt werden.

Bezogen auf dieses Thema ist das Hauptproblem, dass das Abbauverfahren in den meisten Steinbrüchen auf keiner systematischen Klassifizierung der Gesteine basiert und daher keine selektive Gewinnung erfolgt. Da in der Realität die meisten Abbauverfahren nicht selektiv sind, werden Gesteine mit hoher und niedriger Qualität zusammen gesprengt, bilden ein Haufwerk und werden somit zusammen aufbereitet. Diese Vorgehensweise verursacht Produkte mit unbekannter Qualität, die unvorhergesehene und unerwünschte Auswirkungen bei der zukünftigen Verwendung haben können.

Durch die Entwicklung eines Analyseverfahrens auf Basis der zwei Parameter LOI und MAG ist die Online Bestimmung der Qualität von Gesteinskörnungen, die als Gleisschotter und im Asphalt verwendet werden, möglich. Die oben genannten Parameter sind in drei verschiedenen Steinbrüchen erfolgreich überprüft worden. Basierend auf den jeweiligen Verwendungszweck konnten Grenzwerte für die beiden Parameter bestimmt werden.

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Clausthal, October 2015
Alireza Tayebi

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1 Introduction

Concrete, rail ballast, asphalt and road construction all have one thing in common: natural crushed stone aggregates. Based on the definition presented by the "Geological Society of London" aggregates are defined as particles of rocks which, when brought together in a bound or unbound condition, form part of the whole of an engineering or building structure [1]. In civil applications, "natural aggregates" are the most wanted materials and their consumption in construction purposes is growing every day. This is a reason why today this field is getting more competitive. Because of these facts, a doubt in the "quality" of the products is becoming the most decisive factor in selecting a specific supplier. Meeting the demanded standards in each country is vital in order to get the permission of utilizing these crushed stones. To conform to these standards, the existence of an exact definition of the possible encountered hazards, a tested proofing technique and, a continuous quality management are the key factors to be on a safe side.

Natural crushed stone is one of the most applicable materials in construction purposes and its supply and demand increases every year. Based on the market research, the world´s demand forecast for construction aggregates will increase by 5,8% annually and reach 53,2 billion metric tons in 2017 [2]. Asia/Pacific region is the dominant market [2] . There is rapid growth between 2012 and 2017, China alone will account for over half of all new demand from this region [3]. The estimated amount of crushed stone production in future reveals this fact-it is the most wanted and needed raw material extracted from the earth. Since our resources are limited, for a sustainable development and optimal exploitation of them, supervision of their quality is inevitable.

1.1 Quality management

The world today is heading to a new concept: Globalization. The idea of globalization causes the companies to be in the path of continuous technological innovations. Without gradual advances in the field of technology, they will lose their market share to their competitors. Therefore, the companies have no choice other than to speed up with this wind of change in order to meet the new challenges. This kind of situation and ambience brings up chances and threats. Therefore, the organizations have to come up with new discoveries and innovations as well as fulfilling operational perfections.

This goal is achieved through a continuous management of quality. In ISO 8402-94 standard quality is defined as: “The set of characteristics of an entity that give that entity the ability to satisfy expressed and implicit needs.” The ISO 9000:2000 standard describes quality as “The ability of a set of intrinsic characteristics to satisfy requirements” [4] and quality management (QM) is the way to be certain that the desired service/product meets the demanded requirements and quality. In other words, quality management is about improving processes to make it good and work smart, so that a better job at a lower cost and with less labor is done [5]. There are two main aspects to quality management [5]:

- ✓ Product or service design and,
- ✓ Operating and running smarter.

In order to gain the following goals it is considered that QM has four essential components as shown in figure 1. Improving our operation through the following stages will enhance the process by saving money, time and the best product deliverance.

Figure 1: Building blocks of QM [6]

Quality control (QC) is one of the most important compartments of QM. To achieve an acceptable quality control, different methods are used. For our study purpose, the quality control of the wanted products will also be examined through a QC approach.
To have a better understanding of the project for which its quality shall be managed, the problem must be defined. Describing the problem (which a solution is expected for) will lead to a better project quality management where not only the quality of the project but also the quality of the product is dealt with.

1.2 Problem definition

Natural crushed stones known as “construction aggregates,” have a wide range of usage in civil applications. Railway, road, and structure/infrastructure construction are three main application groups of the aggregates. To ensure longevity of products and service, igneous rocks are mainly used for the above-mentioned purposes. They simply show a higher strength and abrasion resistance and that is why they are more preferred in the civil engineering field.

The problem with igneous rocks is that in some cases these rocks tend to break down and disintegrate. This breakage or disintegration is sometimes up to a complete loss of structure or in other words their full degradation. This problem has direct impact on the quality of the downstream products such as railroad ballast and asphalt.

Since in most of the applications, aggregates are fundamental components of the end product (such as asphalt, railroad ballast and concrete) the quality management of aggregates is crucial. In this research project, I will scrutinize asphalt and railway ballast applications. To be more accurate, we will look at the consequence of degradation phenomenon in two different aspects as follows:

I. Railway ballast

   Crushed stones used for railway ballast may disintegrate and sometimes completely degrade resulting in reduction of track ballast strength.

II. Asphalt

   Low quality aggregates (which break down with time) in asphalt cause problems, such as increase in swelling, reduction in compressive strength and, reduction in indirect tensile strength. These problems will then lead to the phenomenon named “stripping” of asphalt concrete.

Solving these issues and presenting a solution needs a deep understanding of the problem. We have concluded a complete detailed study on this topic in order to figure out this worldwide quality problem of the crushed natural stones.

In order to cover the aforementioned topics, (the core of) this thesis is divided into two parts: the first part deals with the quality of railway ballast and the second part with quality of asphalt. Each section has its own specifications and related experiments.

2 Scientific, technical and economic problem definition

2.1 Overall outlook

Aggregates or more precisely construction aggregates are the most mined raw materials in the world [7]. The construction aggregates may include a wide range of coarse material, such as sand, gravel, crushed stone, and recycled concrete/asphalt. Their specifications have made them an important ingredient of many civil engineering operations. Their strength factor has brought the aggregates to composite materials such as concrete and asphalt. Because of their hydraulic conductivity, they are widely used for drainage purposes. Their load bearing characteristic and stability made them suitable for road/railroad construction purposes as a base material [7].

Natural crushed stone is a type of construction aggregate. The large amount of crushed stone´s yearly production and consumption in form of aggregates in different constructional applications shows their high importance in the building industry. In order to have a better understanding of their importance in our everyday life it is referred to figures 2 and 3 [8].

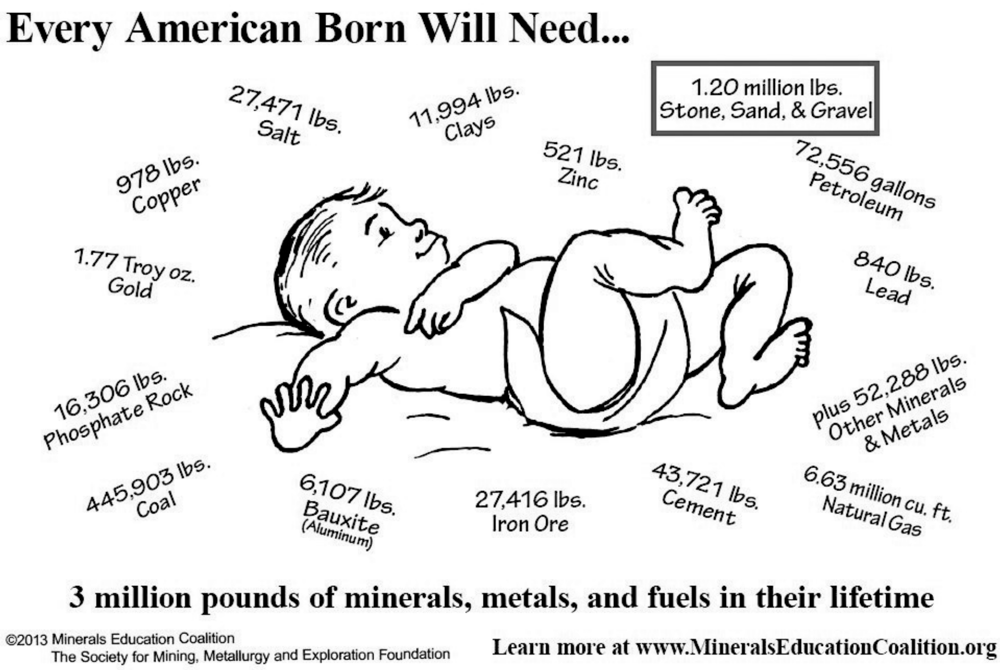


Figure 2 : Material consumption of an American person during her/his lifetime [8]

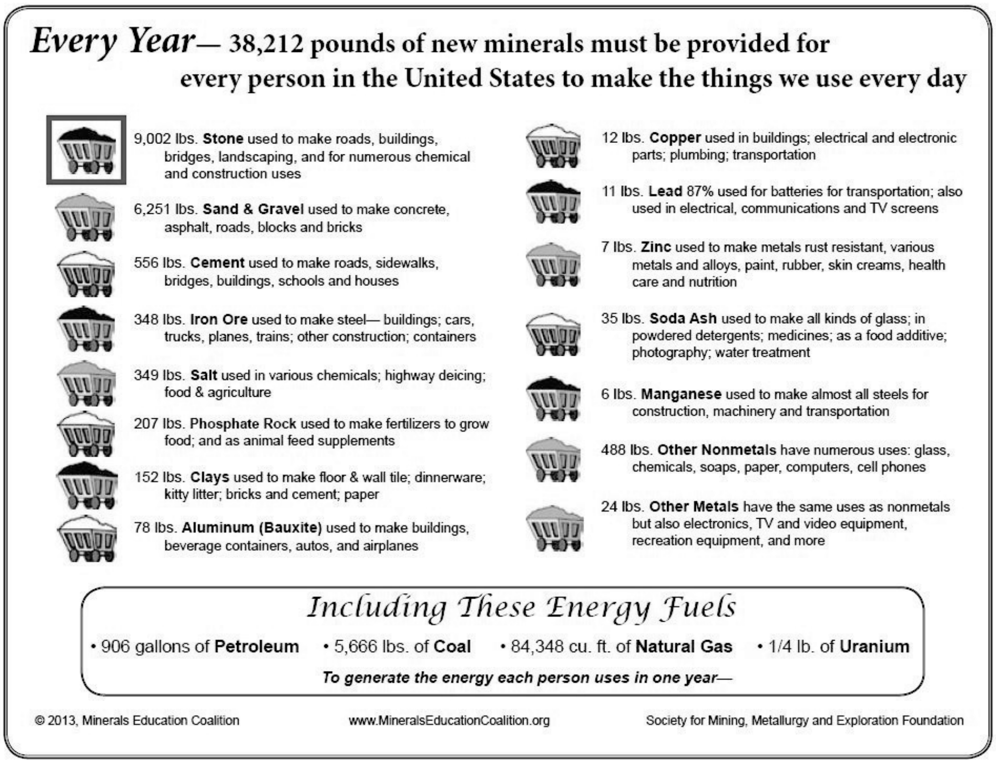


Figure 3 : Material Consumption per capita in America [8]

The world consumption of aggregate exceeds 40 billion tons per year and in Germany a yearly amount of about 350 million tons of natural crushed stone is produced for civil engineering construction purposes [9]. A great deal of this amount is from magmatic rocks due to their particular specification, such as high strength, stability and wear resistance with respect to other types of rocks. That is why they are preferably used for road construction, concrete production, railway construction, and hydraulic engineering. For each usage, the materials must meet specific criterion.

2.2 Advanced problem definition

Igneous rocks such as basalt or andesite are broadly used as construction material for buildings, railways, monuments, roads, hydraulic structure. Therefore, their durability is a crucial prerequisite and essential for their utilization and lifetime safety determination. As an example for hydraulic constructions, a minimum survival of 100 years and for monuments up to a millennium is needed. Durability is a function of mechanical and chemical stability of the rock, which result from the phase composition and fabrics of the rock. By chemical and mineralogical studies, the existence of less stable rock-forming constituents can be determined.

The quarry industry is confronting an enormous problem regarding the durability of the rock and its resistance aspect. Some igneous rocks (based on their texture and composition) demonstrate a tendency to fast chemical weathering, alteration, and finally mechanical decay [10] [11]. The problem is that this alteration and weathering process has impact on the engineering properties and behavior of the rocks and it is not easy to distinguish the tendency of such rocks to disintegration and decay with time, from their fresh form during mining activities. During daily mining operation, the rock might present a satisfying and well mechanical property but by progression of time, the degradation process may proceed to a point of complete and quick rock destruction and decay. This is exactly the case that some quarries are facing right now (figure 4). With this outlook, the durability of the rock should be the dominant criterion in quality requirements and assessments. On the other-hand are the petrological aspects. In the sense of petrology, the quality of the (basaltic) rocks is a complex function of mechanical and chemical stability of the rock-forming materials and components. Since rock is not homogenous and the conditions in which rocks are formed and cooled down are different (heterogeneity of circumstances), therefore the quality of the basalts differ from place to place of any geological formation. The scale of this variability is a matter of meters to even centimeters. Crushed and degraded zones (because of hydrothermal alteration or chemical weathering) are normally related to tectonic faults, joints, spacings, and interfaces with other geological formations [10].

In quarries with geologically heterogeneous regions, the use of selective mining method is strongly recommended. However since most quarries do not apply any selective mining techniques, therefore high quality and poor quality rocks are blasted simultaneously, mixed together in a muck-pile and consequently are crushed together leading to the production of qualitative inhomogeneous aggregates. These types of products may not provide the desired properties or in other words, they could fail to have acceptable geotechnical qualities for further applications such as railway ballast and asphalt.

To be able to select high quality construction materials, early recognition of the tendencies of rock decay is required which is not simple. The quality of rock is a function of physical and chemical properties, and the rock behavior is defined over time.

Direct contact of basaltic rocks with water leads to clay mineral formation. Existence of clay minerals (montmorillonite, chlorite, kaolinite, serpentine, illite, vermiculite, smectite,…) plays a significant role in deterioration process [10] (many researchers believe that the determination of smectite content of basic igneous rocks shall be considered as either the main factor of durability assessment or it shall be regarded as a major input for durability prediction calculations [12]). Different factors such as rock-water contact, available surface area, and environmental conditions (pressure, temperature, and pH) govern this process. The type of clay mineral, which is formed because of water-rock interaction, depends on the composition of the rock and the dissolved ions in the solution [10].

The clay minerals are either present in the rock structure from its origin or due to the water-rock interaction; they are steadily formed (from the less stable rock forming constituents) by different processes during the whole geological history of basalts. Even in un-altered fresh rocks, a minimal quantity of clay mineral may be found (formed in post-volcanic stage). Water plays an important role in basaltic rock decay and deterioration. The basaltic rocks are formed either in a dry environment or in a wet medium. If they are formed by solidifying from the volcanic lava, then they contain some water or water vapor which will saturate the cracks, voids and fine pores (the lava itself has some minor quantity of water). If the basaltic rocks are solidified in a wet environment or under seawater condition then a great amount of water is entered to the rock structure. This causes heterogeneous cooling which causes internal stresses and tensions and will lead to the formation of micro cracks and fissures. Therefore, space for the formation of clay minerals is available. In the next phase, the water-rock interaction, transvaporization (water content) and the further saturation of cracks and voids with hydrothermal fluids, the alteration of less stable constituents of the rock happens and consequently secondary clay minerals are formed. If the host rock is basalt, the result of the hydrothermal alteration would be hydrothermal clay minerals such as chlorite, smectite and serpentine mineral group. Thus, in brief form, the basalts that originate in a wet environment, uptake extra water from their wet surroundings favors the reactions of less stable constituents. Pushed up water enters and penetrates the rock along the cracks, fractures, spacings, and empty voids, which means besides the surface weathering, hydrothermal alteration zone also takes place along the crushed and fragmented zone of the volcanic rock masses. The rock bodies from such regions normally show more heterogeneity and less durability from themselves. These zones are optimal for the formation of secondary clay minerals [10].

The amount of secondary clay minerals formed in fresh rocks depends on temperature and water content. Retention time, drainage, and surface area govern the rate of the alteration. The quantity of the clay minerals shows in which environment the rock solidified. Considerable amount of clay minerals reveals wet or sub-aquatic condition and little fractions represent dry condition [10].

Natural processes are a function of time and the rate of the rock alteration process is comparatively slow. The surface of the rocks or aggregates is full of abundant broken bonds. When water molecules which are strongly polar are in contact with these surfaces, then reaction starts and different anions (silicate) and cations (alkali metals, alkali earth metals) are liberated and react together to form the aluminosilicates. Cations like Na^{+}, K^{+}, Mg^{+2}, Ca^{+2} and Al^{+3} are the best ones to compensate the lack of charges (and balance the charge) of silicate [10].

Since surface area plays an important role in controlling the rate of alteration, therefore any kind of decrease in the grain size (e.g. milling, crushing, and fracturing) could result in enhanced formation of clay minerals. For example when clay minerals such as smectite are formed, because of its swelling pressure, steady rhythmic expansion and shrinkage, they noticeably contribute to deterioration of mechanical strength which results in degradation, disintegration and decay of the rock (as most of the clay minerals, smectite is sensitive to humidity and water and starts to swell) [10]. If such materials (containing smectite clay minerals) are consumed as construction aggregates, especially in structural layers of roads, the smectite content of the aggregates is released during process preparation, construction, and in-service which causes an increase in the plasticity of the materials. This results in the weakening of the structural road layers leading to premature asphalt failure [13].

Experiments have shown that synthetical formation of clay minerals is possible by grinding and milling the rock under water condition. This is due to a change in chemical and mineralogical nature. The generation of clay minerals shows the tendency to a faster alteration. Immediate water-rock interaction leads to a fast rate of the reaction, which is because a high value of cross sectional area is presented to the system. An example could be the transformation of magnetite to hematite by grinding and oxidation (under wet conditions). This phenomenon will also cause asphalt quality problems as about 30% of asphalt concrete is made of fine particles.

2.3 Main objectives

To overcome this old problem of the related industry, a concrete list of objectives must be defined. The following items have to be guaranteed in order to present a useful long-term solution:

1- Quality of the natural crushed rocks (as construction materials)
2- Ranking of the aggregates and crushed rocks for different industry usages
3- Determination and guarantee on long-term behavior of the crushed rocks

To obtain the above-mentioned targets, we shall define and develop a novel systematic testing-technique. Our most important objective is to be able to quantify the long-term durability of the aggregates for civil engineering applications.

In this research work, we will look at two different industrial applications of aggregates, namely railway ballasts and asphalt concrete.

2.4 Railway ballasts

An essential and indispensable requirement for sustainable and economical production and further processing of crushed natural stone is their compliance with the required product quality. The durable stability, permanent high strength and structural stability of these products is of utmost importance for their application in construction operations.

As a result of a time-dependent loss of stability/structure of the natural stone after usage in civil applications, the natural stone producer may encounter devastating economic consequences. The following reclamation comes with a great economic implication. The hidden problem is that the level of the reclamation surely corresponds to a multiple of value of the delivered natural stone. Actually, in comparison to the small benefits from natural stone products´ sale, the costs of mining and further processing (including the construction) are very high.

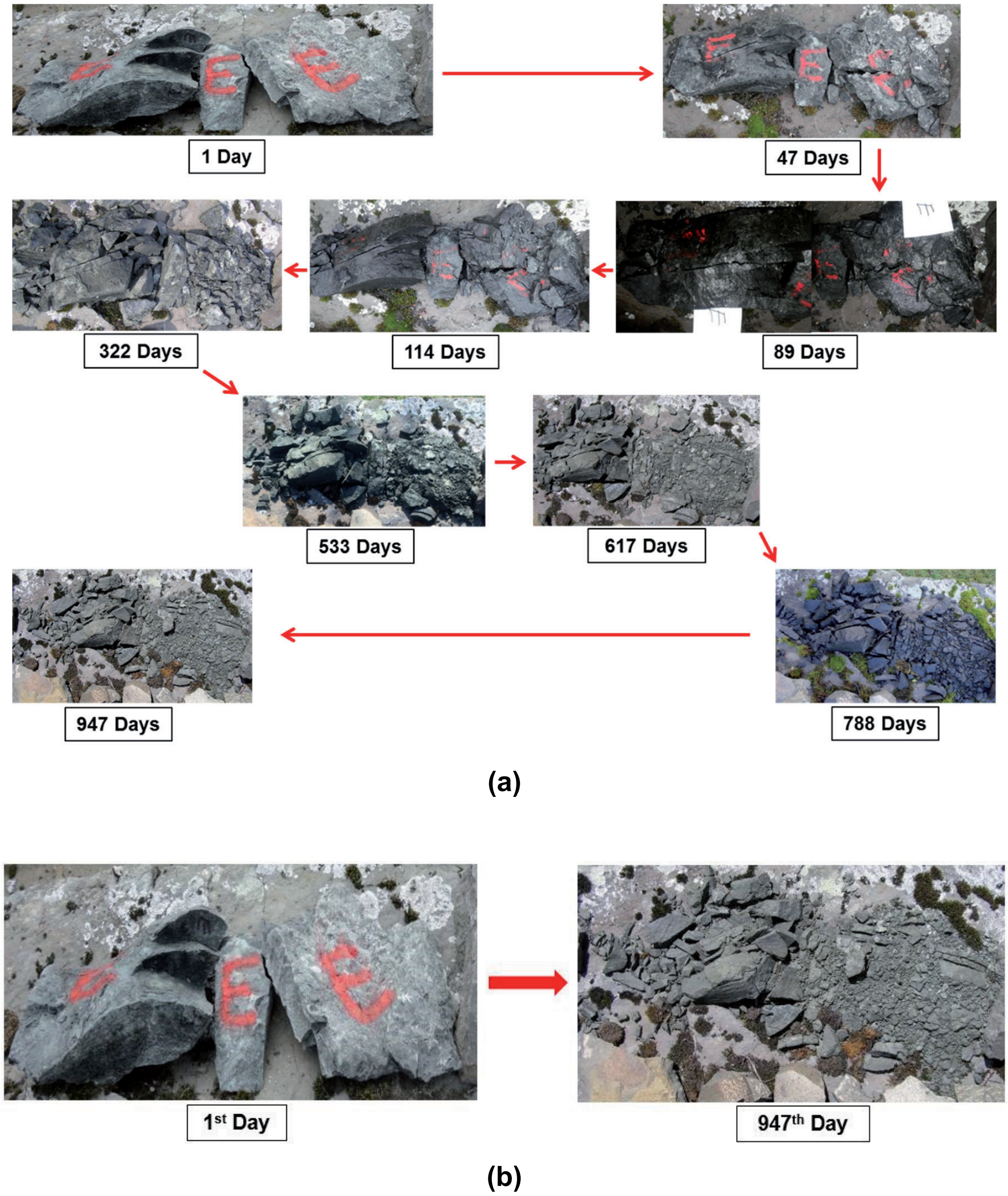


Figure 4 : Magmatic rock before and after disintegration, (a) in detail, (b) short-cut

In Germany the reclamations from the road construction area, especially asphalt and railway track production as well as the railway ballasts are always on the daily agenda (basis). Customers hardly block production line of a specific product because of repetitive reclamations.

The aforementioned serious problem is valid for the magmatic rocks. In fact, these rocks will lose their strength or structure stability with the passage of time, when they are exposed to outside weather under atmospheric conditions. The main problem is that sometimes it cannot be recognized from the fresh shape of the rock that it is going to disintegrate later. A company, which is encountering rock products with partially or completely low quality, is not in a position to make a decision about the aimed quality sorting/controlling. Furthermore it shall be considered that the production of different rock size fractions (aggregates with different sizes) through drilling and blasting where thousands of tons of mined material is produced from the deposit, reveals the scope of this problem even more clear. The blasted muck pile shall then be examined for the subsequent degradation potential, which is an impossible task.

The development of a technique or procedure, which is fast, unique in its results, possible in implementation at the mine site and able to be integrated in production, is undoubtedly one of the greatest challenges in this industry.

2.5 Asphalt concrete

The asphalt paving industry is responsible for the construction of world´s asphalt motorways, highways, streets, airport runways, parking areas, driveways, coastal protection, canal lining, reservoirs, footpaths/cycle paths, sport and play areas [14]. Asphalt comprises of about 5% bitumen and 95% mineral aggregates [15] [16] [17] and aggregates contribute up to 90% of asphalt pavements [9].

More than one billion tons of asphalt is yearly produced for the above-mentioned purposes [14] [18]. About 275 million ton of this amount is produced in Europe by around 4700 asphalt plants and is used for the European road network which consists of about 70000 km of classified motorways [17] [19] [20] [21] [22]. In Germany the annual asphalt production accounts for around 50-60 million tons which is manufactured and produced by more than 300 companies [23] [24] [25]. The total amount of motorway network in Germany is 12879 km, which is ranked as the 11th place in the world [26] [27]. To ensure a long-life service of the streets, the quality of asphalt is a necessary requirement, which is also crucial to the economy and profitability of this branch of industry. Despite all technical efforts, so far no satisfactory result is obtained. Permanent repairs of the roads and expressways, which includes the older asphalt surfaces, and very often the fresh and newly asphalted streets, points to and emphasizes this problem. The extent of this problem is sometimes so that the asphalt surface layer must be removed from several kilometers of new asphalt road.

The direct/indirect economic consequences of such low quality asphalts or early loss of quality types of asphalts is enormous.

Due to the very high importance of this issue, asphalt quality improvement is a focus of the research and development (R & D) section of the respective industry associations and research institutions.

Figure 5 : Asphalt problems due to low quality asphalts (stripping and raveling of asphalt)

3 State of the art

3.1 Railway ballasts

The time-dependent loose of structure which happens in natural stones or natural stone products is mainly regarded as “chemical weathering” or “alteration” in technical papers or industrial professions. In case of basaltic rocks, it is very often called as by its German word “Sonnenbrenner” (in English as “sun burn”). Regardless the different terms, they all deal with the same problem, i.e. certain magmatic rocks (after they are mined and used in civil constructions) independent from the time, start to lose their structure, degrade and in extreme cases disintegrate. This shows similar characteristics as unconsolidated rocks. It shall be noted that usually only some parts of the deposit is affected by this problem. Prior selection of the low quality rock is usually not possible and therefore influences the quality of the whole deposit.

3.1.1 Common weathering and quality indices

According to state of the art, the following methods (described in subsequent sections) are used internationally in order to determine the structural loss of natural stones or in other words to specify the aggregate qualities through their alteration degree. In European test methods, the following Norm/DIN/Standards shown in Table 1 are applied to aggregates and natural stones.

Table 1: DIN Standard applied to aggregates and natural stones

Test type	Standard
Tests for general properties of aggregates	DIN EN 932-1 to DIN EN 932-6
Tests for geometrical properties of aggregates	DIN EN 933-1 to DIN EN 933-10
Tests for mechanical and physical properties of aggregates	DIN EN 1097-1 to DIN EN 1097-10
Tests for thermal and weathering properties of aggregates	DIN EN 1367-1 to DIN EN 1367-5
Tests for chemical properties of aggregates	DIN EN 1744-1 to DIN EN 1744-3
Natural stone test methods	DIN EN 12371

- **Natural weathering test**

In this method, the trend of deterioration of the natural rocks is evaluated. The rock samples are placed outside for a period of time (for example one year). Therefore, they are exposed to a natural weathering process. After a period of time, the secondary and primary situations are compared with each other and the change in weight is controlled.

- **Determination of “loss on ignition” (LOI)**

The “LOI” is the amount of volatile substances in a material or rock sample. By this test, not only the water content (free water molecules as humidity and crystal-structure binding water) is evaporated but also the emission of CO_2, SO_2 will take place as the carbonate/sulfate compounds start to decompose. In higher temperatures, this process also affects the clay minerals. The loss on ignition is introduced by some researchers as an index for degree of weathering, the lower the LOI value the lower is alteration and weathering and vice versa [28] [29] [30] [31]. As the weathering grade increases, the water uptake (H_2O^+) will arise because of hydration and clay minerals´ formation (the clay minerals are known for having a large amount of water in their crystal structure). The LOI reflects the quantity of H_2O^+ in a sample; the higher the LOI value the more H_2O^+ is bound through hydration and clay formation. Therefore, the LOI index is sensitive to weathering and is known as a “chemical weathering index” [29] [32] [33] [34] [35] [36] [30] [37]. As will be discussed later on, this index will be used as an indicator for the determination of natural stone quality.

- **Proof of “Smectite-Analcime” existence**

The existence of clay minerals in a magmatic rock is regarded as an indicator for the tendency of the rock to degrade and disintegrate. In case of the presence of smectite in combination with analcime at the same time in a rock, it is assumed that the rock has a higher deterioration potential. It may be noted that a general weathering feature in basaltic rocks could be defined as the formation of secondary minerals with predominance of smectite, which is deleterious for the rock quality [38]. Clay minerals formation process and the effect of clay minerals on rock durability are briefly discussed below.

The existence of clay minerals in different igneous rocks (such as basalts) with various quantities is mentioned in many publications [11]. In general, clay minerals are formed within the whole geological history. The very first clay minerals were formed in early post volcanic period after intrusion/deposition. Since lava has some water in itself, this water is then either incorporated into some silicates such as mica and amphibole or as steam that will cause hydration of less stable constituents such as olivine. As a result of this hydration, smectite, chlorite, vermiculite and serpentine are formed. If the intruded/deposited lava is cooled down in a wet environment, then water uptake takes place and the formation of hydrothermal solutions occur which causes further alteration of the rock forming materials. By this type of alteration, the primary minerals are dissolved and the precipitation of the secondary minerals in the fissures and voids takes place. Two major processes could be defined regarding this issue: dissolution along the cracks and precipitation inside the cracks, which causes expansion and loosening of inter-granular bindings. As a matter of fact the formation of secondary minerals (including clay minerals), reflects the composition of migrating liquids and environmental conditions. The process of crystallization of clay minerals inside the tiny voids often generates high pore pressures. Therefore, the crystal structure of the main primary mineral undergoes severe mechanical deformations that results in the formation of micro-fissures and micro cracks, which leads to the deterioration and disintegration of the rocks [11].

- **Magnesium sulfate/Sodium sulfate "soundness" test**

This test is a type of "soundness" test and its main aim is to simulate the freeze-thaw procedure. By repeatedly immersing the rock sample in magnesium sulfate or sodium sulfate solution, the solution will enter and precipitate inside the pores and cracks of the rock sample. In the drying process (dehydration phase) the salt inside the pores starts to crystallize and therefore imitate the water expansion in the freezing process. This crystallization generates pore expansion (through the expansion force) and at the end causes the rock to degrade. Based on the researches, since the test results of the two salts might be significantly different, thus this method is used in combination with other indicators as an evaluation criterion [39] [40].

- **Rock "petrographic" characteristics**

As complimentary information about the disintegration tendency of the natural stones, the study of the petrographic properties of the rocks with the help of X-Ray Diffraction (XRD), thin and polished section microscopy may be mentioned. These factors provide mineralogical and textural characteristics of the samples. In this case, the XRD device detects the presence of clay minerals or other deleterious minerals. The microscopy analysis of thin/polished sections is also used to determine the existence of secondary minerals to evaluate the potential of the rock to disintegrate.

- **Inquiry on physical conditions**

Measurements of porosity, density, and water absorption ability are also used as some indicators for assessment of the deterioration potential of natural stones. In this context, the unconfined compressive strength (UCS) is partially employed as a measure.

- **Test method for thermal and weathering properties of aggregates-part 3: Boiling test for “Sonnenbrand Basalt” (DIN EN 1367-3:2001-06)**

“Sunburn” or its German equivalent “Sonnenbrand” is a characteristic of basaltic rocks, which leads to their disintegration. The first stage of sunburn is distinguished by formation of the so-called “spots” on the surface of the rock. Then an irregular system of “capillary cracks” develops between the spots and finally destroys the basaltic rock [41]. Analcime (usually formed in the cracks) and nepheline are the constituents of basaltic rocks. The accumulation of the analcime and their transformation (analcime to nepheline) creates stress and further more causes micro cracks to be developed. The concentration of these micro cracks then end up to the formation of the spots on the surface [42].

“Boiling test” is a standard procedure of identifying this phenomenon [43]. The principle of this method is based on analyzing the changes to rock hand-pieces or aggregates after a cooking process of 36 hours in distilled water. The tendency of the aggregates to loose structure is mainly recognized through color change of smooth surfaces and the subsequent stability studies. In case of aggregates, they will also go through the same test method and their tendency to disintegrate is determined through measurement of mass loss and change in strength (strength reduction on boiling). Never the less it shall be mentioned that the boiling test does not guarantee the sunburn prediction [44].

- **Ethylene Glycol Index (method for testing stone for expansive breakdown on soaking in Ethylene Glycol, CRD-C 148-69, 01.03.1969)**

In this test [45] the samples are placed in glycol solution up to a couple of days. The swelling capable clay minerals (especially smectite and montmorilonite groups) react with glycol and as a result, a volume increase will take place in clay minerals.

This increase in volume is the consequence of organic-clay bond, which is larger than the clay mineral itself. This phenomenon leads to a multiple volume expansion of the clay mineral and finally will cause the rock to disintegrate. Of course this break down occurs if the reaction between the ethylene glycol and the clay minerals takes place. However, the amount of clay minerals, their distribution, and ability to react with ethylene glycol are some of the decisive factors. This test tries to simulate the freeze-thaw process, which takes place in nature [46] .

To assess this process, we will discuss it in a more detailed manner. What really happens is that the saturation of basic igneous rocks with clay mineral content in ethylene glycol ($C_2H_6O_2$) affects the characteristics of the basal spacing (d-spacing). It dissolves the interlayer cations of phyllo-silicates and leads to further expansion of the mineral [12]. Ethylene glycol solution is absorbed by the interlayers of smectite clay minerals and increases the interlayer spacing from 14 A° up to 18 A°; in another word the ethylene glycol test, has impact on smectite group and causes them to expand [13]. A novel method named “modified ethylene glycol durability index” (mEGDI) is recently proposed for the aim of gaining more accurate and trustable results [13] [47].

- **Methylene blue test (Tests for geometrical properties of aggregates-Part 9: Assessment of fines-Methylene blue test DIN EN 933-9:2009)**

This is a type of adsorption dye test [48] which as mentioned in the title (DIN) is for assessing and tracing harmful fines, especially the clayey or cohesive fines in the aggregates. This method studies the reaction of methylene with the swell-able clay minerals (such as kaolinite, smectite, montmorillonite, illite and vermiculite) in the aggregates. Methylene could be used as an indicator when there is need to ascertain the existence of some specific clay minerals in the rocks. For this test, the sample must be milled (to the size of smaller than 125 µm) and then mixed with methylene solution. The milled powder could react with methelyne. In case of reaction, the Na^+ and Ca^{2+} ions of the clay minerals are replaced with the methylene ions and as a result a blue color (in case of kaolinite and illite) or purple color (for montmorillonite) solution is formed. The ground samples may include different amount of clay minerals and based on the extent of their clay minerals (and because of their fineness and particle charges), they are able to absorb more/less amount of dye. A low value of methylene consumption could mean low swelling activity or higher durability and vise-versa. Positive experience of this method is reported in the field of smecite detection in fracture fillings, discontinuities, and thin slip zones [49] [50] [51] [39] [11] [52].

Although in Germany the determination of the tendency of a natural rock to degradation is partially followed by this method, but it is generally considered that this test is less suitable for detecting the rock disintegration property. This is in conformity with our own experiments.

- **Weathering Index**

Chemical/physical weathering is an inevitable process, which takes part in the nature and affects a large number of engineering specifications of the rock mass. Because of considerable technical and economic problem due to structural loss of magmatic rocks, based on various conditions, different types of indices were developed to present the quality of the rocks. In most of these methods, the ratio of the rock forming oxides is generated. The quality of the rock is specified by comparing the calculated indices with an empirical determined range of the same index value. The calculation of this index requires a multi-elemental analysis of the test sample. Table 2 presents a number of the most known weathering indices developed in the recent decades [53] [54] [55] [56] [57] [58] [59] [33] [31].

Table 2: Most important weathering indices largely used and known ([60] [61] [62] [63] [64] [65] [34] [66] [67] [68] [69] [32])

Weathering Index	Index	Formula	Optimum fresh value	Optimum weathered value	Presented by
Product of Weathering Index	PWI	$[SiO_2/(TiO_2+Fe_2O_3+SiO_2+Al_2O_3)] \times 100$	> 50	0	Souri et al. (2006) [60]
Weathering Index of Parker	WIP	$[(2Na_2O/0,35) + (MgO/0,9) + (2K_2O/0,25) + (CaO/0,7)] \times 100$	> 100	0	Parker (1970) [61]
Chemical Index of Weathering	CIW	$[(Al_2O_3/Al_2O_3+CaO+Na_2O)] \times 100$	≤ 50	100	Harnois (1988) [62]
Chemical Index of Alteration	CIA	$[(Al_2O_3/Al_2O_3+CaO+Na_2O+K_2O)] \times 100$	≤ 50	100	Nesbitt and Young (1982) [63]
Plagioclase Index of Alteration	PIA	$[(Al_2O_3–K_2O/Al_2O_3+CaO+Na_2O–K_2O)] \times 100$	≤ 50	100	Fedo et al. (1995) [64] [65]
Loss on Ignition	LOI	$[H_2O^+]$ content of sample (in wight %)	———	———	Sueoka et al. (1985) [34] Jayawardena (1993) [66]
Product Index of Reiche	PI	$[(SiO_2)/(SiO_2+TiO_2+Fe_2O_3+FeO+Al_2O_3)] \times 100$	———	———	Reiche (1943) [67]
Ruxton Ratio	R	$[SiO_2/Al_2O_3]$	10	0	Ruxton (1968) [68]
Vogt's Residual Index	V	$[(Al_2O_3+K_2O)/(MgO+CaO+Na_2O)]$	< 1	Infinite	Vogt (1927) [69]
Mobiles Index	I_{mob}	$1 - [(CaO+Na_2O+K_2O)_{weathered\ rock} / (CaO+Na_2O+K_2O)_{fresh\ rock}]$	———	———	Irfan (1996) [32]

3.1.2 Discussion on the aforementioned conventional methods for detecting the disintegration characteristics of natural stones

Regardless of the reliability and quality of all of the above mentioned methods, it shall be noted that according to state of the art, all these methods concentrate on individual hand-pieces which are to be examined in the laboratory with a great deal of effort. Exploitation by means of drilling and blasting involves large-scale movement of often highly (qualitative) heterogeneous deposits. From pure statistical point of view, the result of examining a hand-piece sample cannot represent the whole deposit or in other words, it may not provide us with a representative result for the whole deposit. The current methods are very time consuming and deliver the test results within few days after the sampling date. The above-mentioned problem will even increase and will more serious, because shortly after the rock is mined, it is subjected to further processing and finishing procedures which takes place in the processing plant.

Almost none of the current methods provide us with reliable reproducible quantitative results. Frequently two different methods deliver us two various results related to the rock quality, as an example we can mention the boiling test according to DIN EN 1367-3 and methylene blue absorption method according to DIN EN 933-9.

As a result of the above discussed methods it shall be noted that, the existing methods are not sufficient and the need for an economical, inexpensive, fairly quick and accurate method to determine the quality and durability of natural construction materials and aggregates is still there [11]. That is why the development of a quantitative and qualitative approach for pre-recognition of this phenomenon and categorizing the natural rocks based on the new classification system is of our great interest. It is desired that this method shall be able to distinguish and identify the variations within the aggregate source [12].

A part of the current research is mainly based on a phenomenon, which is regarded as “alteration” in geo-chemistry. In simple words, alteration is the conversion of primary minerals in a rock into secondary minerals such as clay and carbonates. Alteration is followed up by a change in the basic mineralogy of the rock, which may be a variation in the crystal/textural structure of the mineral while the chemical composition stays the same or in a way that the chemical composition of the mineral is changed. This process is mainly a function of temperature and pressure.

3.1.3 Basics of alteration & hydrothermal alteration process

Alteration is the chemical change and decomposition of lithology units and minerals under pressure, time, and temperature gradient. The alteration refers to a process in the magmatic or post magmatic phase of the rock formation, which takes place due to high temperature/pressure and the circulation of aqueous solutions (hydrothermal alteration). In fact, it deals with the transformation of minerals under the influence of different parameters namely pressure, temperature, time, composition of the primary rock, composition of the fluid, and finally the relationship between the last two factors, which causes changes in the composition of the rock as well as increment of the secondary minerals. This change in composition (or change in mineralogy of the rock) is mainly followed by a mixture of the following processes: hydrolysis, hydration, reduction, oxidation and carbonation which are the result of rock interaction with a hot liquid source (hydrothermal fluids).

As an example, the basaltic volcanic rocks could be chloritized by magnesium rich solution. Chloritization of igneous rocks usually takes place in hydrothermal environments. As a result, phyllosilicates like Biotite, chlorite and serpentine are formed. To describe it in another way, because of hydrolysis process mineral compounds such as Feldspar (primary minerals) are converted to clay minerals (secondary minerals). Therefore, the solution (through ion exchange process) will be richer in sodium and potassium. Usually as a transformation of mineral constituents, different clay minerals e.g., kaolinite, montmorillonite, illite, smectite, sericite are formed (e.g. alteration of K-feldsapr to muscovite by hydrolysis, then further alteration of muscovite results in kaolinite formation which is a clay mineral). Free quartz, limonite, hematite, and goethite are the products of magnetite´s transformation. These minerals replace magnetite in different stages of oxidation process. The conversion and formation of minerals is often accompanied by the addition of OH^- ions. Thus, alteration is associated with an increase in the proportion of volatile components or in other words an increase in loss on ignition value.

Hydrothermal alteration is one of the most important types of alterations. The hot solution or “hydrothermal fluids” (or also called “aqueous solution”) in their way to the top (earth crust) pass through nearby empty spaces, holes, spacing, joints and fracture of igneous rocks causing an alteration in their chemical composition. This passage is always combined with ion exchange process. The hydrothermal alteration, which is actually a chemical alteration, takes place through adding, removing, or redistribution of the chemical components. Because of this process, the hydrothermal fluids are highly concentrated in terms of minerals and metals, and transport different metallic ions. Therefore, the movement of hydrothermal solution through the cracks, pores and fractures of igneous rocks, creates a pregnant solution; rich in different ions and metals (thus, permeability plays an important role in the displacement of the hot aqueous solution). The pregnant solution is then displaced to another location, while taking all these elements with it. Therefore, the vicinity of igneous rocks to this thermal solution causes reduction, oxidation, carbonation, hydration and hydrolysis of rock contents (namely alteration). Since most of the hydrothermal solutions are weakly acidic, the reaction with rock is mostly followed by hydrolysis which simply means the addition of hydrogen and removal of other cations from the rock [70] [71] . To have a better idea about these processes, a small description of each is given here [70] [72] [73] [74] [75] [76]:

- **Simple hydration:**

Hydration is defined as the chemical combination of water molecules with specific minerals leading to a change in structure. Hydration is a type of chemical reaction where water molecules affect the mineral (structure) and as a result, a new hydrated mineral is formed. A popular example is the formation of gypsum which is the result of addition of water to anhydrite (water enters the crystal structure of anhydrate and therefore a new mineral namely gypsum is formed). Hydration of feldspars to clay minerals is another example. Hydration causes swelling and volume increase of the minerals. This is one of the most common processes in the nature and works with secondary minerals such as aluminum oxide, iron oxide, and gypsum. Some minerals such as montmorillonite are capable of absorbing a great deal of water without any particular changes to their structure. Some examples of hydration process are:

$Fe_2O_3 + H_2O \longrightarrow 2FeOOH$ (rare)
(Hematite, red) (Geothite)

$2Fe_2O_3 + 3H_2O \longrightarrow 2Fe_2O_3.\ 3H_2O$
(Hematite, red) (Limonite, yellow)

$CaSO_4 + 2H_2O \longrightarrow CaSO_4.\ 2H_2O$
(Anhydrite) (Gypsum)

- **Oxidation:**

Oxidation deals with loss of electron and in case of minerals; it is the addition and combination of oxygen with minerals. Oxygen could be present in atmosphere or dissolved in soil water. Since oxygen has the second highest electro-negativity within elements, it can cause other elements such as iron, calcium, magnesium, sodium to undergo oxidation process (oxygen is an oxidizing agent and is reduced). Oxidation process is more active in the presence of moisture and causes formation of hydrated oxides. Underneath are a number of examples of this type of reactions.

$$2Fe_3O_4 + H_2O \longrightarrow 3Fe_2O_3 + 2H^+ + 2e^-$$
(Magnetite) (Hematite)

$$4Fe_3O_4 + O_2 \longrightarrow 6Fe_2O_3$$
(Magnetite) (Hematite)

$$2Fe_2O_3 + 3H_2O \longrightarrow 2Fe_2O_3.\ 3H_2O$$
(Hematite) (Limonite)

- **Reduction:**

Reduction is the reverse process of oxidation, which means electron is gained. This is a process of removing oxygen from the minerals. Reduction takes place when the soil is saturated with water (waterlogged condition) or in case of excess water. As an example, the equation below is referred:

$$2Fe_2O_3 - O_2 \longrightarrow 4FeO$$
(Hematite) (Ferrous oxide)

- **Hydrolysis:**

Hydrolysis is a kind of chemical reaction, which takes place in presence of water. In this type of reaction, the chemical bond of molecule is broken down with the use of water molecules. The water molecules (H_2O) are automatically ionized and dissociated into H^+ (hydrogen cations) and OH^- (hydroxide anions). The other compound or mineral will also dissociate in presence of water. Since water is polar and the electro-negativity of oxygen is very high, the minerals/compounds are ionized and broken down. Then the H^+ and OH^- combine with the existing ions in the solution and the minerals, causing decomposition of crystalline structure and formation of new minerals and compounds. Because of this process some positively charged ions such as Fe, Mg, Ca, Na, K will be available. In case of hydrothermal alteration, these ions are spread in the solution and then displaced with it to other locations.

Hydrolysis is the most important process in alteration, which occurs in presence of water. It causes the weathering resistant minerals to be less resistant. One of the typical forms of this reaction is the hydrolysis of orthoclase (alkali feldspar) to clay minerals, quartz and some elements such as Na, K, Ca. In figure 6, the alteration of orthoclase to kaolinite (clay minerals) as a consequence of hydrolysis is presented in a graphical way. The reaction leading to this phenomenon is as follows:

$2KAlSi_3O_8 + 2H^+ + 9H_2O \longrightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+$
(orthoclase + water $\longrightarrow$ kaolinite + silicic acid + potassium)

The hydrolysis of orthoclase or plagioclase feldspar could also result in the formation of sericite (takes place usually in places, which are subjected to hydrothermal alterations).

$2H^+ + 3KAlSi_3O_8 \longrightarrow KAl_2(Si_3Al)O_{10}(OH)_2 + 2K^+ + 6SiO_2$
(orthoclase $\longrightarrow$ sericite + quarz)

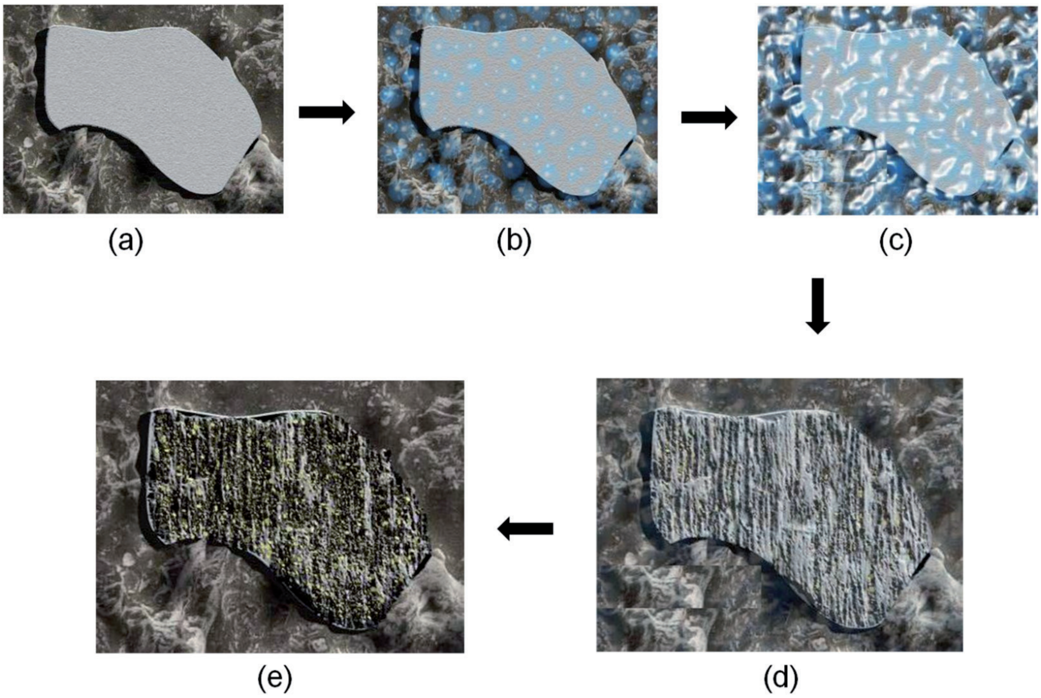


Figure 6 : Alteration of potassium-feldspar to clay minerals [74]

(a) Fresh and unaltered orthoclase (K-feldspar)
(b) Water in contact with orthoclase
(c) Reaction of water and orthoclase mineral
(d) Entrance of water through the rock surface and its cracks, leaching out different ions from the mineral
(e) Formation of clay minerals (yellow) as a consequent of hydrolysis (reaction of water with mineral ions)

Since sodium, potassium, calcium, and iron are important elements in the aforementioned reactions, a brief description on their characteristics is mentioned bellows:

Sodium and potassium are alkali metals. They have very large atomic radius, low electro-negativity, high reactivity, and try to form ionic compounds. Most of their compounds and salts are soluble in water. Na and K react with water to form a soluble hydroxide. This high solubility causes them to be leached easily by water. Calcium is an alkaline earth metal, low electro-negativity, large atomic radius, tends to form ionic bond, reacts rather slowly with water but insoluble in water (it reacts with water slowly because it is partly protected by the insoluble $Ca(OH)_2$). Iron exist in two forms, iron II (ferrous) and iron III (ferric) , where Fe(II) is quite soluble in water in any pH and Fe(III) is soluble only in pH less than 3,5. Iron oxides are insoluble in water but iron hydroxides (rust) are soluble in water. Iron does not have a high electro-negativity and tends to form ionic bond [77] [78] [79] [80] [81] [82].

3.1.4 Types of hydrothermal alteration

Hydrothermal alteration affects the mineralogy of the rock and brings changes to the primary chemical composition, affecting the physical and chemical properties of the mass. The circulation of the hot fluid through the pores and cracks of the rock mass causes a kind of equilibrium between the solution and the rock. It could have impact on a region, district, or the whole ore-body. In other words, the alteration process could have influence from mm to km range. Composition, temperature, pressure gradients are the most influencing factors, which cause the decomposition of the ore minerals and their alteration [83]. Because of hydrothermal alteration, different resources of metallic ores are created [70] [71]. Figure 7 Presents the different hydrothermal alteration zones created as the fluids passes through its way up [84] [85].

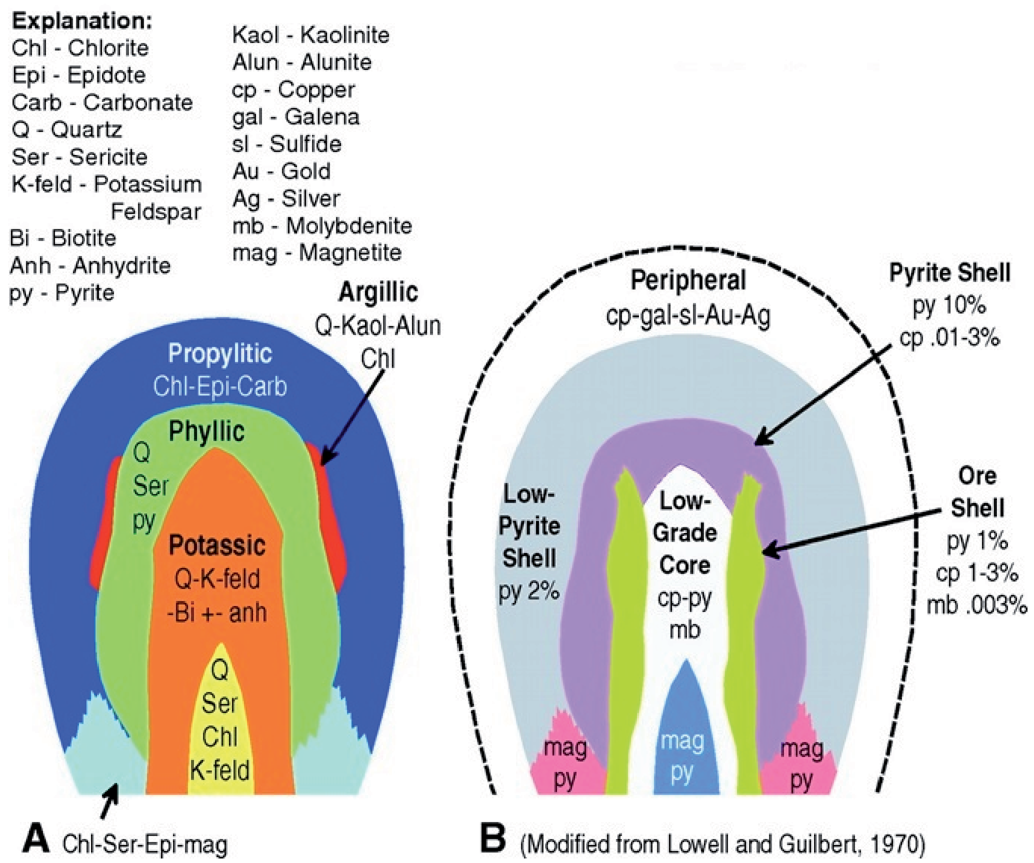


Figure 7 : Hydrothermal alteration zones and minerals [84]

(A) Schematic cross-section of hydrothermal alteration minerals and types, and (B) Schematic cross-section of ores associated with each alteration type

As seen in figure 7, hydrothermal alteration has different types such as propylitic, phyllic or sericitic, argilic and pottasic. It is arranged outward from a potassic core (earliest) to phyllic, argillic and propylitic zones [84]. Each zone has its own characteristics and minerals, which are formed under a specific condition namely composition, physical condition/permeability of host rock, chemistry, pH, Eh, temperature/pressure of the fluid, and pressure/temperature of the location [70]. Alteration zones at depth, in the outer part, consist of chlorite, sericite, epidote and magnetite mineral assemblage and in the inner zone quartz, sericite, chlorite and K-feldspar [84]. A summarized description on each zone is described below [70] [86] [84]: The characteristic minerals of ***potassic*** alteration are quartz, potassium feldspars, biotite, anhydrite and sericite (clay minerals are absent and chlorite might be present in its minimal amount). Potassic alteration zone is identified by the substitution of primary minerals such as sulphides (like pyrite and chalcopyrite) and magnetite by secondary minerals such as biotite, k-feldspar, quartz, and sericite. Inclusion of iron and magnesium brings the formation of biotite or chlorite to consideration. The generation of magnetite and hematite is also common.

Phyllic alteration is an assemblage of quarz, sericite and pyrite minerals and it is the most common alteration type. Plagioclase and orthoclase are altered to muscovite. Since sericite is the characterized mineral of this type of alteration, ***sericitic*** alteration is the other name for phyllic alteration and it is also regarded as sericitization.

Argillic/advanced argillic alteration is recognized through the formation of clay minerals. The mafic and plagioclase minerals are substituted by the clay minerals causing the formation of kaolinite, montmorillonite, illite, alunite and chlorite (this process is developed through extreme base leaching of alumino-silicates, mainly leaching of alkalis and calcium). Kaolin is the more common reaction product. In case of advanced argillic alteration, the whole component of the rock may be replaced by the clay forming minerals. Argillic alteration is a fairly intense alteration.

Propylitic alteration is typical for mineralogical assemblage of chlorite, albite, epidote and carbonates while sericite, pyrite and magnetite may also be present. This is a low-intensity type of alteration and chlorite is the dominant mineralogical phase in prophylitic alteration. Plagioclase generally remains fresh and quartz is unaffected.

As the alteration proceeds, certain assemblage of minerals and compounds are formed. They are sometimes seen together and sometimes there exist no co-occurrence between them, which means the formation of one minimizes the occurrence of the other. Figure 8 presents the summary of hydrothermal alteration assemblages.

If we want to characterize different types of alteration processes to different rock types, then it shall be noted that sericitization, argillization are the typical alterations of felsic (e.g. rhyolite, granite) rocks. Sericitization, propylitization, chloritization and carbonatization (the formation of carbonates of various elements such as iron, magnesium, calcium by means of carbon dioxide rich hydrothermal fluids) are the most predominant alteration types of intermediate (e.g. andesite) and mafic (e.g. basalt) rocks [83].

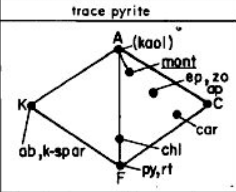
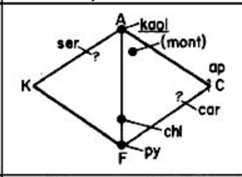
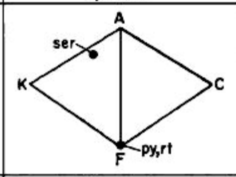
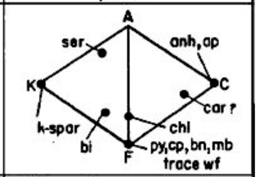
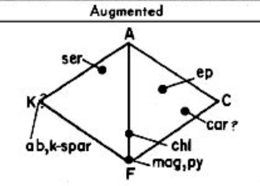
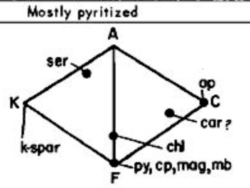
SHALLOW–MODERATE DEPTH ASSEMBLAGES				
FRESH QM, PORPHYRIES	PROPYLITIC ZONE	ARGILLIC ZONE	PHYLLIC ZONE	POTASSIC ZONE
Quartz	No Change	Augmented	Augmented	Augmented
Orthoclase–Microcline	No Change	Flecked with Sericite	Sericitized	Recrystallized, in part replaced by alteration K-feldspar–quartz
Plagioclase (An_{35-45})	Tr. Mont, flecks & granules ep, zois, car, chlorite, kaol.	Montmorillonite → Kaolin	Sericitized	Fresh to completely replaced by brn-grn alt'n biotite, K-spar, ser.
Biotite	Chlor, zois, car, leucoxene	Chloritized, + leucoxene, qtz	Sericite, pyrite, rutile	Fresh or recrystallized to sucrose brn-grn granules, ± chlorite
Hornblende	Ep, car, mont, chlor (2 types)	Chloritized	Sericite, pyrite, rutile(?)	Biotite, ± chlorite, rutile
Magnetite	trace pyrite	Pyritized	Pyritized	Pyritized
A–K–C–F A = Al K = K, Na C = Ca salts F = Fe, Mg				
Veinlet Fillings	Q-cal- K-spar-chlor-rare ab–rt	Q–ser–py–chlor	Q–ser–py	Q-K-spar–bi–ser–anhy–cal–ap
DEEP–LEVEL ASSEMBLAGES				
	OUTER		INNER	
Quartz	Slightly Augmented		Augmented	
Orthoclase-Microcline	Dusted with trace sericite		Alteration K-spar with sericite, relicts common, minor quartz	
Plagioclase (An_{35-45})	Dusted with sericite, chlorite, epidote		Sericitized, with alteration K-spar-quartz, relicts uncommon	
Biotite	Largely chloritized, minor epidote mag added		Chloritized, rare primary relicts	
Hornblende	Chlorite + Epidote + Carbonate		Chloritized; trace carbonate	
Magnetite	Augmented		Mostly pyritized	
A–K–C–F A = Al K = K, Na C = Ca salts F = Fe, Mg				
Veinlet Fillings	Q–mag–py ± Q–ser–cal envelopes		Q–K-spar–ser–chl, tr mag, py, cp, mb	

Figure 8 : Hydrothermal alteration´s types and different mineral assemblages (alteration changes on AKF-ACF diagrams) [84]

3.1.5 Advanced discussion on hydrothermal alteration

The transformation of anhydrous rocks (igneous and volcanic rocks) to hydrous material (clay minerals) takes place when there is a chemical interaction between water and rock. In this process, the water molecules (in form of H^+ and OH^-) enter the mineral structure [87]. The alteration of basalts and conversion to clay minerals is also followed by this phenomenon. The circulation of hydrothermal water and subsurface water accelerate this process. The two environmental parameters namely the amount of water available to react with the rock (water to rock ratio: W/R) as well as the atmosphere (chemically open or closed system) are also crucial. With the same initial composition of the rocks, some factors such as water chemistry (e.g. pH), thermodynamic variables (temperature and pressure), and kinetic parameters for mineral formation determine which type of alteration mineral will be produced. The mobility of the elements during alteration process is a function of above-mentioned items, therefore based on the alteration environment different individual mineral assemblage may be produced [87].

Rocks with similar composition and altered under different conditions, may show distinctive chemical changes due to the characteristic of the alteration environment. The interaction between water and the rocks leads to alteration of thermodynamically unstable primary minerals such as olivine, pyroxenes, and feldspar and formation of new stable minerals (e.g. clay minerals). For example in case of basalts (as in figure 9), the alteration could lead to the generation of different compounds and mineral assemblage. The key parameters as mentioned above are the water to rock ratio and chemical system condition (open or close to atmosphere) [87].

In figure 9, the colored areas are the alteration trajectory of basalts. As it is clear, in case of low water to rock ratio and in open system (purple color) the magnesium and alkali cations are removed and the primary minerals in the rock are replaced with aluminum clays and iron oxides. In other words, basalts tend to alter to Al-clays. During the process of clay formation, the liberated and transported cations may form a salt. In case of low water to rock ratio and closed system (orange and green), the primary minerals are replaced with Fe, Mg clay minerals and oxides [87].

In the subsurface closed systems, water is isolated from the atmosphere and the chemical equilibrium is achieved through precursor-rock chemistry. Temperature and pressure are the main factors, which rein the resulting alteration mineral assemblages. In this area the water to rock ratio is generally low (W/R<1) and other influencing factors such as redox, pH and ion activities are determined on the local scale within the rock pores and cracks. Aqueous phase reacts with mafic rocks and results in an anoxic and alkaline fluid. The transportation of soluble ions is limited and that is why the alteration is mainly iso-chemical, which means that the bulk mineralogy of the rock changes but the elemental abundance remain almost constant. Therefore, the altered rock differs slightly with the parent rock in the sense of elemental abundances. In systems with negligible sulfur content, the alteration of the bulk rock may result in the formation of iron oxides and iron (II)/magnesium, chlorite and serpentine. However, in open systems and close to the earth surface, the aqueous phase is in contact with atmosphere and the atmosphere has impact on some parameters such as pH, redox, and ion exchange of the fluid. At high water to rock ratio (W/R>1) the vicinity of three decisive factors namely water, iron (II) and atmosphere leads to oxidation and hydrolysis of iron (II) which produces iron (III). These processes contribute H^+ ions into the solution and form an acidic pH fluid. When this oxic fluid (with moderate pH) is in contact with basalt, leaching process takes place. Silica, chlorine, sodium and potassium are highly soluble and therefore mobile, magnesium, calcium and sometimes silica are relatively mobile, whereas aluminum, iron (III) and titanium are immobile. Hence, as chemical weathering proceeds, the rock decomposes and the chemistry of the remaining rock becomes more aluminum rich. The leaching process alters the mafic lithologies to aluminum clays (e.g. kaolinite and montmorillonite) and iron oxide assemblage. In next phase, different salts (chlorides, carbonates and sulfates) may be precipitated from the pregnant solution. In case of open system and low water to rock ratio (W/R<1) olivine dissolves at first, since it is the primary soluble phase. This means the depletion of magnesium and iron, but the parent rock is slightly altered [87].

Insufficient surface water (in open-system) delays the leaching process and formation of clays and salt assemblages and on the other hand inadequate subsurface water for hydrothermal circulation decreases the kinetic of alteration process. As a result, the availability of water is an important factor for the alteration of minerals and rocks and low water to rock ratio delays the transportation of the ions [87].

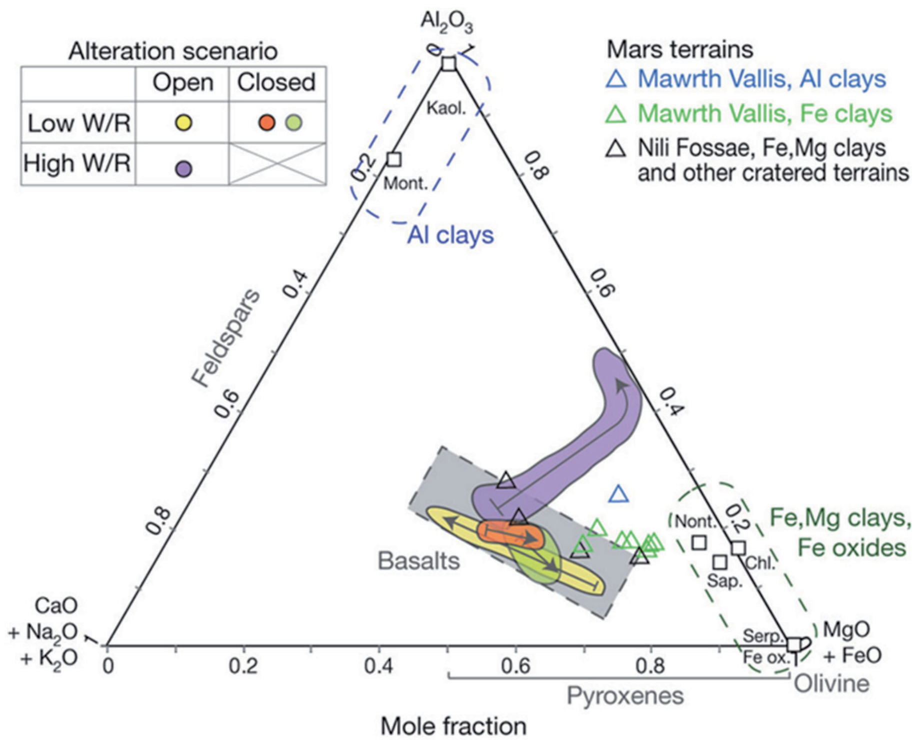


Figure 9 : The existence of chemical and mineralogical changes during hydrothermal alteration process of basalts [87]

3.1.6 Serpentinization of rocks

Serpentine minerals or serpentine group are actually the greenish/brownish minerals that are formed from serpentinization and found in serpentinite rocks. They are hydrous magnesium iron phyllosilicate minerals with universal formula of $X_{2-3}Si_2O_5(OH)_4$ where X is Mg, Fe^{2+}, Fe^{3+}, Ni, Al, Zn or Mn. Thus, the complete formula is: $(Mg,Fe,Ni,Al,Zn,Mn)_{2-3}(Si_2O_5)(OH)_4$ but the more used form is $(Mg,Fe)_3Si_2O_5(OH)_4$. Their greenish color is because of the presence of olivine. The serpentine minerals are rich in magnesium and normally the chemical analysis of a serpentine sample shows up to 90-95% of SiO_2, MgO and H_2O [88] [89] [90] [91].

The most famous minerals of this group are (polymorphs of serpentine): Antigorite $(Mg,Fe)_3Si_2O_5(OH)_4$, (Népouite $((Ni,Mg)_3(Si_2O_5)(OH)_4)$, Chrysotile $(Mg_3(Si_2O_5)(OH)_4)$, lizardite $(Mg_3(Si_2O_5)(OH)_4)$. Antigorite is a magnesium-iron silicate with modulated structure, Népouite is a nickel silicate mineral, and when all the nickel is replaced with Mg, then lizardite is formed. Although chrysotile and lizardite have, the same formula but they are different. The Si/Mg ratio is greater in chrysotile. Lizardite consist of planar layers whereas chrysotile cylindrical layers. Lizardite has greater potential of cation (Al^{+3}, Mg^{+2}, Fe^{3+}) substitution. All four minerals have sheet silicate structure and fall into serpentine group (or also called as kaolinite-serpentine group) and known as serpentine [89] [90] [91] [92] [93].

The aqueous alteration of ultra-mafic and mafic rocks is known as “serpentinization”. Silica (SiO_2) content of mafic and ultra-mafic rocks is less than 52%, they are rich in iron and magnesium, and they bear low calcium and potassium content. Olivine and pyroxene are the main rock forming minerals of these types of rocks (mafic and ultra-mafic) which mean they are rich in iron and magnesium and low calcium and potassium content (that is why olivine and pyroxene are known as ferromagnesian silicates). The high content of Fe and Mg causes their color to be dark [94] [95].

Serpentinization is the reaction of mafic and ultra-mafic lithologies (olivine and pyroxene rich rocks) with water. This reaction produces brucite, magnetite, hydroxide, serpentine minerals, and librated molecular hydrogen, which not only is a source of energy but also could be broadly used by microorganisms [96].

Serpentinization is a low temperature metamorphic process in which rich iron-magnesium and low silica content rocks are oxidized (ferrous iron, Fe^{+2}, is oxidized an-aerobically by the protons of water resulting in H_2 formation) and then hydrated with water to produce serpentine. Within this process, considerable amount of water is absorbed to the rock, leading to volume enlargement and structure destruction. Serpentine has a large amount of bound water, which is a considerably thin layer of water surrounding the surface of the mineral. Since water is a polar molecule and its electrical polarity is high (one side with extreme positive charge while the other has strong negative charge) they attract and form bonds not only with each other but also with any other charged surfaces such as soil minerals (in particular clay has high potential to bond with water molecules). This strong bonding and attraction between the water molecules, causes the formation of such an extreme thin water film on serpentine. Serpentine contains around 13 wt.% H_2O [88] [97] [98]. This is an exothermic hydration process, which means water is consumed and a great deal of energy is released as a result of transformation of olivine and pyroxene to *serpentine* and *magnetite*. The amount of heat produced is a function of quantity of in-take water to form serpentine. Just to have an idea, serpentinization consumes about 300 liters of water for each cubic meter of altered rock. At the same time, this process produces 660 000 000 Joules of heat per cubic meter of rock (it means the energy produced by serpentinization of one cubic meter of rock is enough to run a 100-watt light bulb for around 76 days). This process is capable of increasing the temperature of the rock to about 260°C. That is why serpentinization is famous as an energy source production and implied as a source of life [99].

Serpentinization of mafic and ultra-mafic rocks produces hydrogen through oxidation of ferrous iron content of pyroxene/olivine and reduction of water. In other words, H_2 is generated when the process of oxidation of ferrous iron to ferric iron takes place and leads to the splitting of water during olivine/pyroxene alteration. Equation below presents this reaction (olivine could also react with n molecules of H_2O) [100]:

$$3(Mg_{1,8}Fe_{0,2})SiO_4 + 4,1H_2O = 1,5Mg_3Si_2O_5(OH)_4 + 0,9Mg(OH)_2 + 0,2Fe_3O_4 + 0,2H_2$$

During the serpentinization process, the pyroxene and olivine are altered to serpentine, some Fe (II) which is released from the minerals is oxidized to Fe (III) and precipitated as magnetite (normally ferric iron is mainly stored in form of magnetite and its formation is to some extent the consequence of Mg-rich nature of serpentine). Reduction and splitting of water to form H_2 is connected with the oxidation of iron. The total iron remains nearly constant, in some conditions (anoxic) a part of the oxidized Fe (II) forms magnetite and the rest of it enters serpentine and brucite mineral structure. In this case, serpentinization is a stepwise process with an intermediate stage of iron-rich brucite and serpentine formation. In the final stage serpentine, magnetite and H_2 are formed. The final step is dependent on the SiO_2 source. In this case, the reactions are as follows:

Intermediate stage:
$2(Mg_{1,8}Fe_{0,2})SiO_4 + 3H_2O = Mg_{2,85}Fe_{0,15}Si_2O_5(OH)_4 + Mg_{0,75}Fe_{0,25}(OH)_2$

Final stage:
$57Mg_{0,75}Fe_{0,25}(OH)_2 + 30SiO_2\,(aq) = 15Mg_{2,85}Fe_{0,15}Si_2O_5(OH)_4 + 23H_2O + 4Fe_3O_4 + 4H_2$

Because of the dissolution of Fe-rich serpentine and brucite during later alterations, Fe (II) will be released and the system will reduce to a level where H_2O is not stable anymore and splits into H_2 and O_2.

Iron rich serpentine alteration:
$Mg_{2,85}Fe_{0,15}Si_2O_5(OH)_4 + 6H^+ = 2,85\ Mg^{+2} + 0,15\ Fe^{+2} + 2SiO_2\,(aq) + 5H_2O$

Iron rich brucite alteration:
$Mg_{0,75}Fe_{0,25}(OH)_2 + 2H^+ = 0,75\ Mg^{+2} + 0,25Fe^{2+} + 2H_2O$

The ratio of Fe(III) to ∑Fe changes over time. In initial phase the incorporation of Fe (III) is low, then in intermediate phase it is high and in the final stage it will decrease again [98] [100] [101].
Serpentintinization may also take place in presence of carbon dioxide. In this case, out of serpentine and magnetite, either magnesite or methane is also produced. The reactions related to magnesite or methane generation are as follows:

Methane production:
$(Fe,Mg)_2SiO_4 + nH_2O + CO_2 = Mg_3Si_2O_5(OH)_4 + Fe_3O_4 + CH_4$

Magnesite production:
$(Fe,Mg)_2SiO_4 + nH_2O + CO_2 = Mg_3Si_2O_5(OH)_4 + Fe_3O_4 + MgCO_3 + SiO_2$

As above, this process could take up to “n” molecules of water. In case of carbon dioxide and water presence, the serpentine may alter to form talc. Talc is a hydrated magnesium silicate, which results from the metamorphism of magnesian minerals such as serpentine, olivine and pyroxene in presence of water and carbon dioxide (namely hydration and carbonation process). Just like serpentine, talc also has water in its structure. Based on the talc content of a rock, the loss on ignition value may be from 4 wt.% for 95 wt.% talc content up to 27 wt.% for 50 wt.% talc content. Talc is usually categorized in clay mineral group [102].

It shall also be mentioned that the degree of serpentinization is proportional to the density of the rock. The more the density the smaller is the degree of serpentinization of olivine and pyroxene and as the density decreases, the serpentinization arises [101]. Temperature, water to rock ration (W/R), pH and redox conditions are the influencing factors governing this process and have impact on the incorporation of ferrous iron into secondary minerals and H_2 generation. Since water-transport and water-rock reactions usually appear to take place in the discontinuities and fracture zones of the rocks, therefore they are mainly the places where the rock is mostly altered [100].

3.1.7 Aim of the research

It is assumed that two important and substantial driving forces assist in the process of degradation and decay of the rocks. The first one is originated from the structural inner strain of the rocks, which is developed due to shrinkage during the rapid cooling phase, and the second one is caused by reaction and phase transformations of less stable minerals, which are accompanied by volume changes. In the first stage, the release of the inner strains (which also happens during mining operations) creates plenty numbers of micro fissures which open the way for the entrance and penetration of water and other solutions. In the next stage, phase transformation, which coincides with expansion, broaden the existing micro cracks, and develops more abundant micro fissures and obvious visible cracks. The presence of physically and chemically unstable constituents usually leads to these types of transformations. As a result of these two driving forces, the inter-granular binding between the rock forming elements is weakened and consequently the strength properties are diminished and decreased. In reality, both forces act simultaneously causing the disintegration of the rock in a shorter time interval. It shall also be mentioned that mining operation itself also has great impacts on creating cracks and micro cracks within the rock mass body [10] [11] [103].

The existing classical methods of testing mechanical properties of rocks are expensive, time consuming, non-reproducible and not representative. They need accurate sampling and (need) sometimes, sophisticated testing devices. To be able to predict the behavior of the rock mass in time and under fluctuating conditions, complicated testing procedures must be done several times which is very tedious and time consuming. Because of these disadvantages, the demand for testing of rocks in a cheap, fast, and reliable technical process rises. For this purpose, it would be the utmost goal to develop an online method.

The main aim of this particular research is to develop an easy to handle, inexpensive, applicable on-site and rapid qualitative method for the early detection of the structural stability of natural stone (mainly for basalt and andesite). Thus, the technological stages of quarrying natural stone with its various sequences and mass flows must be taken to account. Another point to take into consideration is the ability of this method on performing measurements directly on the blasting borehole locations and right on the borehole cuttings. This will definitely bring immediate results. Natural stone and aggregate industry shall be moved to a position where with its own staff and without large investments on material and human resources, is able to expand the current quality management significantly. Finally, this research project should not only satisfy the goal of optimizing the mineral deposit usage but also should minimize the economic risks of natural stone industry.

3.2 Asphalt

Asphalt is a mixture of aggregates (≈95% by weight), binder (≈ 4% - 5% by weight) and different sort of additives (up to 2% by weight). They are all heated up and mixed together (this is the traditional process of constructing the daily seen asphalt pavements) to form the so called “hot mix asphalt.” Aggregates are the natural crushed stones mined from the quarries. Binder is mainly bitumen, which keeps the aggregates together (like glue). Additive is a kind of chemical material added to the mixture to enhance the overall asphalt characteristics such as stiffness, durability, stability, permeability, workability, resistance to moisture damage, fatigue resistance, adhesion and cohesion (e.g., calcium hydrate, lime stone, aluminum oxide, potassium hydroxide, sodium hydroxide, etc.).

Many different factors are mentioned as the influencing parameters on asphalt expected useful life. Traffic load, climatic conditions such as change in temperature, rainfall amount, and rainwater quality, as well as the impact of the chemicals such as de-icing salts are some of these effective factors. However, a more important influencing parameter namely the adhesion behavior between aggregates and bitumen is specified in almost all recent related publications. The study of the fundamentals of these influencing factors has been the subject of many researches since the thirties of the last century (1930´s). There exist many technical papers and publications including published research reports regarding this topic. Based on the state of the art, the adhesion behavior (at the interface layer between bitumen and aggregate) which is partly grouped under the term “affinity,” is itself a function of other influencing parameters. The attachment of these two components (bitumen and aggregate) together is known as “adhesion.” The chemical and physical bond between bitumen and aggregate surface is a result of the interactions between the two materials. However, to have a better understanding of adhesion, the characteristics of both bitumen and aggregates (as the main components of asphalt concrete) must be precisely declared. The effect of bitumen on adhesion behavior is known through the following parameters: viscosity, chemical composition, ageing resistance, origin of raw oil and polarity. The influence of the mineral (aggregate) is well known by means of; mineralogical composition/formation, surface charge, surface roughness, porosity, surface coating and polarity [104].

Regarding this issue, there are two linguistically synonym words that must not be confused with each other. From technical point of view, there is a huge difference between them and they deal with completely distinct issues. These two words are adhesion and cohesion. The adhesion is a resultant of the attraction molecular forces at the interface of two unlike bodies, in other words it is the bonding between two materials namely an adhesive and a substrate. Cohesion is described as the intermolecular forces within one single body or the internal bonding strength of an adhesive itself. In our case, the adhesion bond is created between bitumen and aggregate whereas the cohesion appears in the binder (here bitumen) alone [105] [106] [107]. Figure 10 shows a better schematic view of this concept.

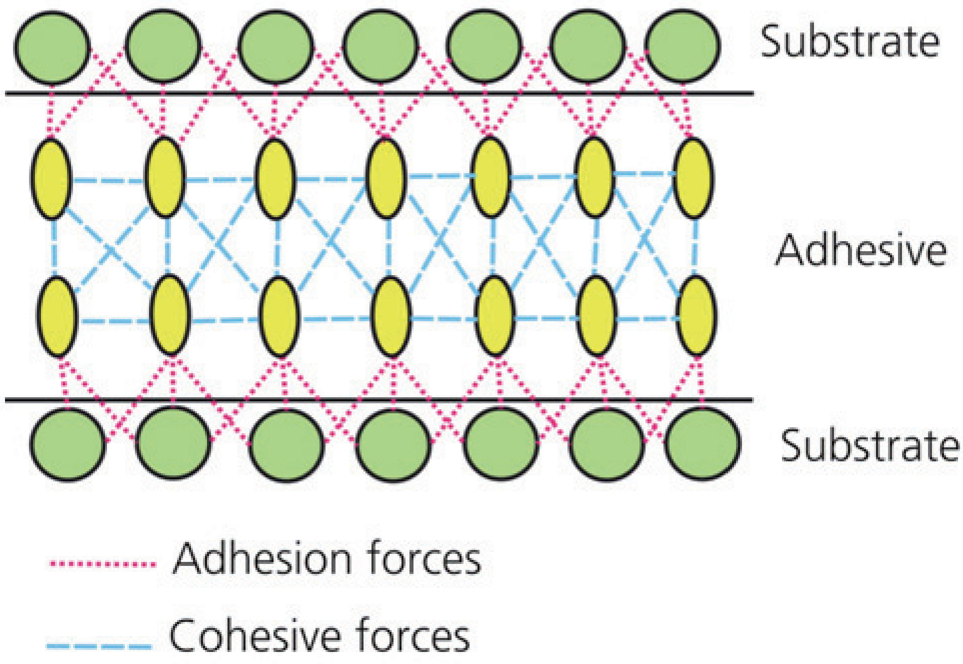


Figure 10 : Schematic explanation of adhesion and cohesion [106]

3.2.1 Cohesion and adhesion failure in asphalt

Actually, the damage to asphalt mixture may be considered from two points of view: cohesive failure, which happens within the mastics of the asphalt or adhesion failure, which is related to the aggregate-bitumen interface. In both cases, the characteristics of bitumen and the thickness of the bitumen around the fine and coarse aggregates are important. The main theory regarding this issue states that asphalt mixtures with thin bitumen films fail in tension because of adhesive bond rupture, whereas those with thick bitumen/mastic films fail because of the damage within the mastic itself. Figure 11 is the graphical view of this theory. In thin bitumen coatings, the adhesive strength governs the total asphalt performance, which means the adhesive bond strength in the presence of water determines the total mixture strength. In case of thick mastic coatings (thicker than the transition point as shown in figure 11), then the cohesive properties control the damage resistance (in this situation, the impact of moisture penetration into the whole mixture itself might be the key to assess the moisture damage of the mixture). In this respect, paying attention to the following points is crucial: (1) how much moisture the mastic holds (the mastic is able to hold a definite mass of water in itself) and (2) the influence of the rheology of this infused water [108].

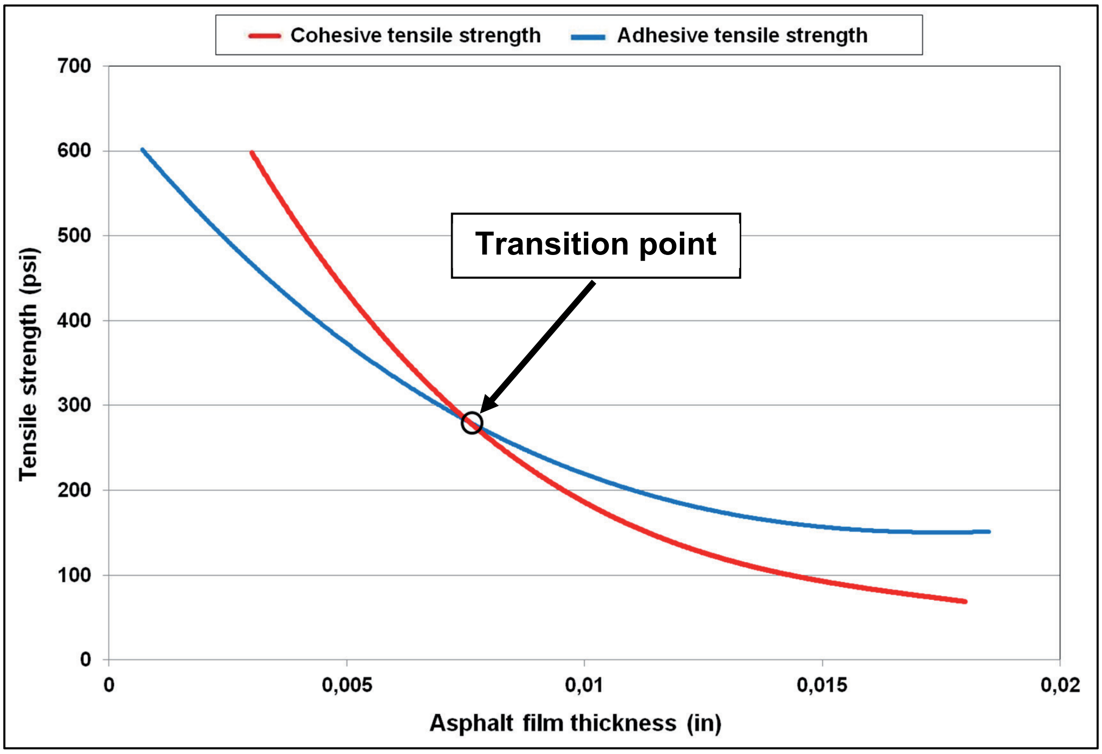


Figure 11 : Adhesive vs. Cohesive bond failure according to bitumen film thickness [108]

Different parameters and factors do have impact on the aggregate-bitumen adhesion. About 80% of these factors are controllable during production and construction. Table 3 presents some of the factors that affect on the affinity of bitumen to aggregate grains.

Table 3 : Parameters affecting the bitumen-aggregate bonding strength [109]

Aggregate properties	Bitumen properties	Mixture properties	External factors
Mineralogy	Rheology	Void content	Rainfall
Surface texture	Electrical polarity	Permeability	Humidity
Porosity	Constitution	Bitumen content	Water pH
Dust		Bitumen film thickness	Presence of salts
Durability		Filler type	Temperature
Surface area		Aggregate grading	Temperature cycling
Absorption		Type of mixture	Traffic
Moisture content			Design
Shape			Workmanship
Weathering			Drainage

Among all the above-mentioned factors, the mineralogical composition of the aggregates is of great importance for us.

The failure at aggregate/bitumen bond is referred as “stripping.” Majority of adhesive failures (affinity problems) have been associated to siliceous aggregates such as granite, rhyolite, quartzite, etc. Actually as a rule of thumb, aggregates with more silicon oxide content (acidic rocks) are more difficult to coat with bitumen, whereas the basic rock such as basalt and limestone are easier. As will be discussed in the coming sections, absolute majorities of the aggregate surfaces are chemically categorized as hydrophilic (water loving) or oleophobic (oil hating) [109].

The physic-chemical properties such as chemical composition, shape, structure, grain size, shape, texture and residual valence are also important for the adhesion process. The surface charge or residual valence is noted as a crucial parameter in many researches. The aggregates with unbalanced surface charges possess a surface energy. If the aggregate surface charge is coated with a liquid of opposite polarity, then the surface energy demands may be satisfied and could result in an adhesive bond. Generally, where two liquids e.g. water and bitumen, are present, the liquid, which satisfies this energy requirement, will generate a stronger adhesion to the bitumen surface. Based on this fact, the phenomenon of stripping bitumen from the aggregate surface in the presence of water could be related to the existence of surface charges as well. The main reason is that water equilibrates the surface charges on the aggregate surface better than bitumen. Therefore, bitumen is separated from the aggregate surface [109].

The physical and mechanical adsorption of bitumen layer on the aggregate surface depends on a number of parameters, namely total volume of permeable pore space, size of pore openings, viscosity, and surface tension of bitumen. The existence of fine microstructures of pores, voids, micro cracks may also help in increasing the adsorptive surface area available for bitumen. The bitumen may be adsorbed to the aggregate surface until a depth of 180 A° (18 nm) [109].

The surface texture of the aggregate, presence of dust on the aggregate surface and the pH of water in contact with bitumen may also affect the bonding between the bitumen and aggregate. The roughness of the aggregate surface is also crucial and helps in gripping the bitumen more tenaciously to the surface. Some believe that the aggregate roughness plays a more important role than the aggregate mineralogy [109]. In fact, one decisive factor with regard to stripping problem is “quality” of the aggregates (based on our own experiments), which is closely related to its mineralogy and the electro-chemistry laws. On the aggregate quality and its different ranking systems, a brief description was introduced in the former sections. Other theories/mechanisms for (describing the) stripping aspect is presented in the following sections.

3.2.2 Asphalt related theories and mechanisms

For a better understanding of existing asphalt problems, selected theories and mechanisms are discussed with respect to asphalt sensitivity to moisture damage and its adhesion behavior. These theories/mechanisms are divided into two main groups: bonding process theories (also known as stripping theories) and separation process mechanisms (stripping mechanisms) [104].
The corresponding theories of bonding process include mechanical theory, chemical theory, theory of molecular orientation, thermodynamics theory. The separation mechanisms consist of displacement, detachment, pore pressure, film rupture, etc.

3.2.2.1 Bonding process theories (stripping theories)

Different theories and assumptions are proposed in order to identify the bonding process between the aggregates and bitumen. Since the adhesion characteristic is the most important property of any bituminous mix, these theories mainly deal with the aggregate-bitumen adhesion concept. A brief description on each theory is given below.

3.2.2.1.1 Mechanical theory

The *mechanical adhesion/interlocking theory* states that the rougher the surface of aggregates, the more effective is the bonding and adhesion between bitumen and mineral aggregates [110] [111] [112]. The rougher surfaces provide higher porosity and therefore more surface area. The roughness increases contact area between bitumen and aggregate (figure 12).

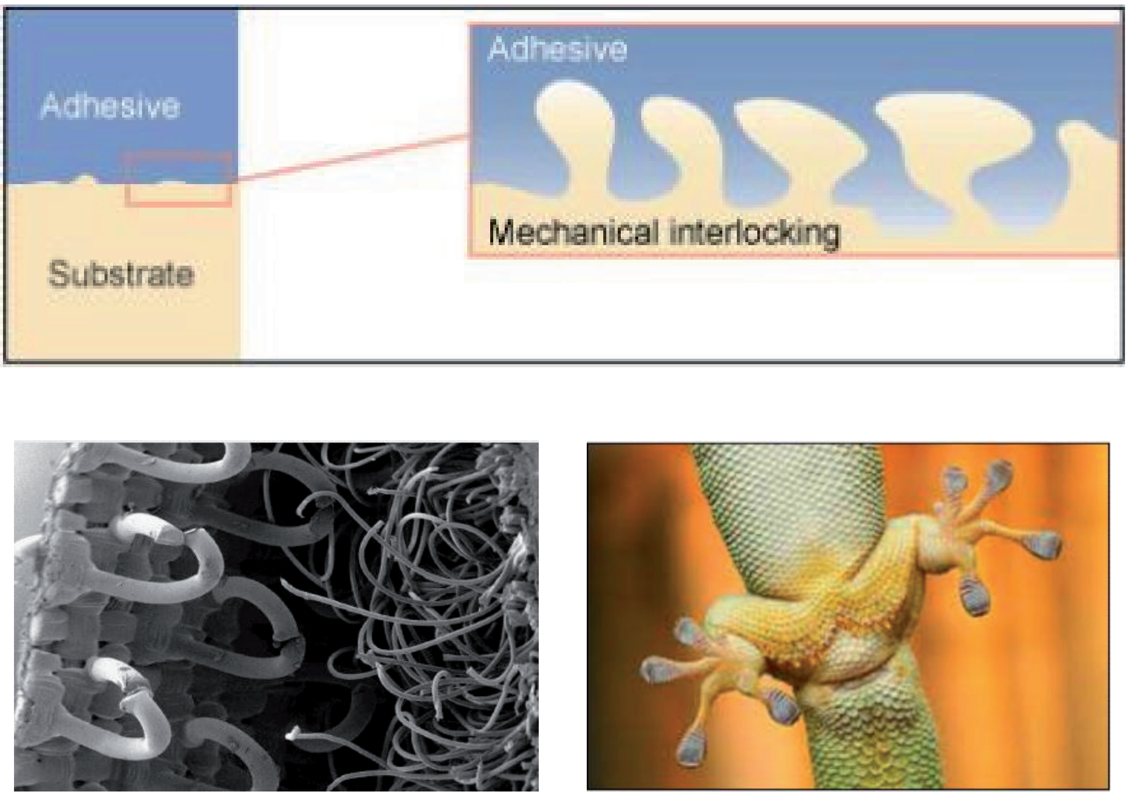


Figure 12 : Concept of mechanical adhesion theory in aggregate-bitumen contact surface [112]

The principal concern dealt in interlocking theory is the mechanical gripping of the binder (bitumen), inside aggregate surface pores, cavities and asperities. Different factors such as aggregate surface texture, aggregate wettability, binder viscosity, aggregate porosity, angularity, surface area, particle size, surface coating and, surface chemistry of binder and aggregate, may have impact on an ideal mechanical adhesion [112].

In this theory, the researchers postulate that surface texture of an aggregate is the responsible factor for adhesion and the chemical bonding and interactions between aggregate and bitumen plays no important role [113]. This theory focuses mainly on physical form of adhesion, which is a function of physical characteristics of aggregates. The aim is to create an aggregate surface capable of maximizing the surface area and such a texture that facilitates a strong physical bond, which may significantly enhance the nature of the chemical bond between aggregate surface and bitumen, even in presence of water [108].

3.2.2.1.2 Chemical theory

The *chemical bonding/reaction theory* is based on the chemical reactions between bitumen and aggregates (figure 13). The postulation of this theory arises from the fact that acidic and basic compounds are present at bitumen-aggregate system and the chemi-sorption mechanism between bitumen and aggregate influences the adhesion. According to the premises of this theory, the acidic and basic components of both sides react together to form a water insoluble compound which resist against adhesion loss and consequently stripping. Based on the literature review, bitumen construct a better bonding (adhesion) with basic aggregates surface rather than aggregates with acidic surfaces [112] [114] [108] [113].

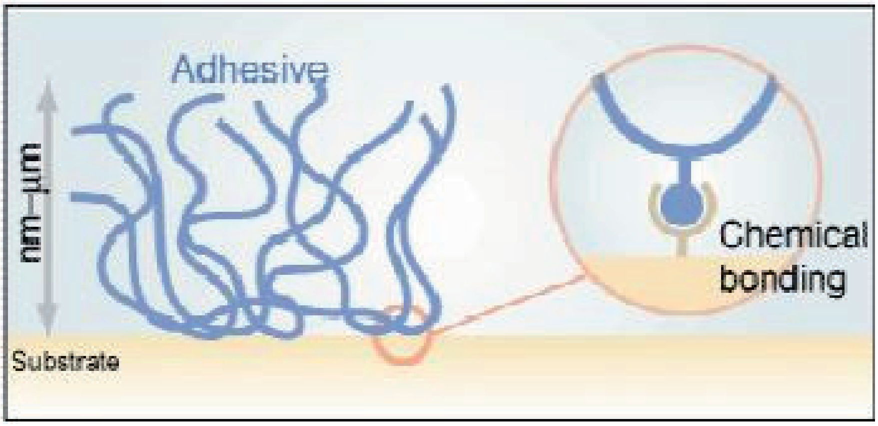


Figure 13 : The formation of chemical bonding between aggregate and binder contact surface area [112].

The adhesion of aggregate and binder (bitumen) is actually a chemical interaction between the two surfaces, which leads to the absorption of bitumen on aggregates surface. This absorption could take place by ionic bonding (in case of polar groups) or “Van der Waals” forces (in case of non-polar groups) [112].

3.2.2.1.3 Theory of molecular orientation/surface energy

The *theory of molecular orientation* or *surface energy* or *electrostatic adhesion theory* is based on the satisfaction of energy requirements of the aggregate surface through bitumen molecules at the interface or bonding (adhesion) surface. When the bitumen and aggregate are in contact with each other, the bitumen molecules orient themselves toward the boundary layer or the interface. Thus, the negative charges of the aggregate surface molecules are neutralized with the positive charges of the bitumen molecules [104] (figure 14). Based on this theory, adhesion is the result of electrostatic interaction between aggregate and bitumen (charged) surfaces. The attraction of different charges leads to adhesion [112]. According to the adhesion theory, the adhesion between the aggregate and bitumen is facilitated through a surface energy reduction on the aggregate surface as the bitumen is adsorbed on the surface of the aggregate [113].

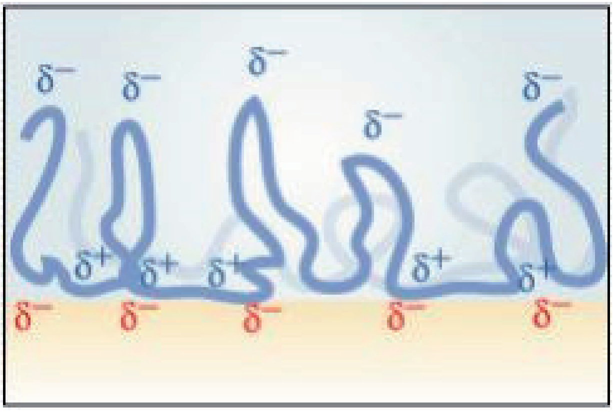


Figure 14 : Distribution of electrical charges at the aggregate-bitumen interface [112]

This theory is also known as surface energy theory. The reason is that surface energy may be described as the relative wettability of aggregate surface by water or bitumen (wettability is briefly described in next section). Due to lower viscosity and lower surface tension, water is a better wetting agent than bitumen [108].
Surface energy is work per unit area [Jm^{-2}] and surface tension is defined as the force acting on unit length (dyne/cm or N/m) and in case of liquids they are identical, e.g. surface energy of water at 25 °C is 0,072 Jm^{-2} and its surface tension is 0,072 N/m (or 72 dyne/cm) [115] [116].
Figure 15 shows the surface tension of a type of bitumen as a function of temperature (in a temperature range of 21 °C to 124°C). The maximum value in this range of temperatures is at 21°C which is ca. 35,5 dyne/cm whereas minimum value is reached at 124°C which is about 18 dyne/cm. As it is depicted, the rise in temperature reduces the surface tension of bitumen, on the other hand the increase in temperature reduces the contact angle of the bitumen resulting in a better wettability of the particle surface

(increase in temperature decreases the viscosity of bitumen as well). It is deduced that the effect of temperature on the surface tension of bitumen is significant.

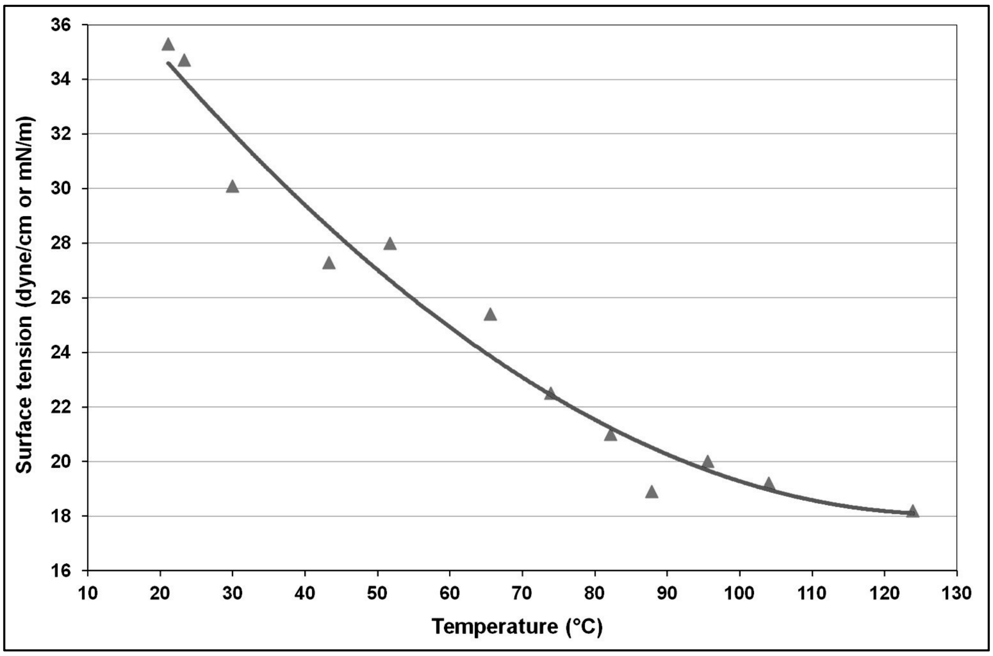


Figure 15 : Surface tension of a type of bitumen in different temperatures [117]

Graph below (figure 16) shows the relationship of surface tension of water with temperature. Water has a surface tension of 72 dyne/cm at 25°C, which arises from polar nature of the water molecules. The increase in temperature causes a significant decrease in surface tension of water. This is the reason why hot water is a better cleaning agent. Hot water has lower surface tension thus a better wetting property in order to get inside the pores and fissures rather than bridging them because of surface tension. Soaps and other detergents have the effect of further lowering the surface tension of water. Therefore, it readily enters the pores [118].

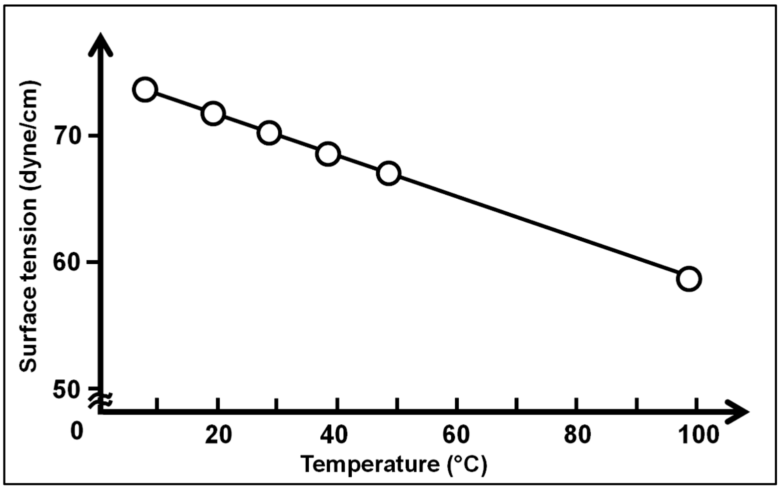


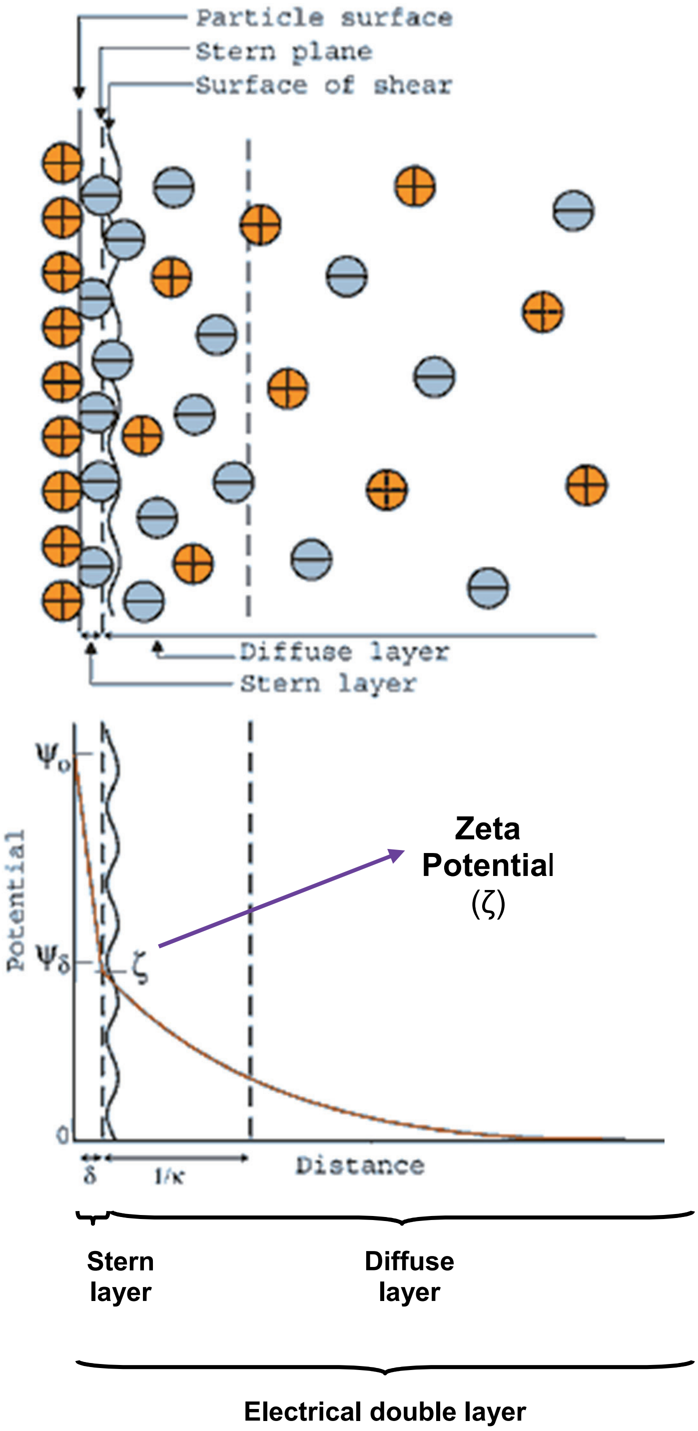
Figure 16 : Effect of temperature on surface tension of water [118]

The existence of polar groups such as OH groups in a substance causes surface tension. The greater the proportion of polar groups in a certain molecule the stronger is the attractive forces between its molecules, which means higher surface tension. In other words, strong attractive forces lead to a high surface tension. The tendency of a liquid to form discrete droplets on a surface (rather than wetting the surface) is also a consequence of powerful attractive forces. In reality if the surface energy of a substrate is less than the surface tension of a liquid coating, then the liquid will not tend to spread over the surface and form a thin layer. By increasing the surface energy of a substance, through the formation of a wet-film over the substrate surface, a better wetting of the surface will take place and a dry-film adhesion is enhanced. To have a better view of this issue, we consider a water droplet on a polished surface table with wax, which is rich in hydrocarbon molecules. The forces that holds hydrocarbon molecules together is much weaker than the forces that act between the water molecules and therefore the water droplet tends to remain in a droplet form [119].

Many researchers couple the surface energy and molecular orientation energy together as a part of one theory, because both of them consider the structuring of bitumen molecules at bitumen-aggregate interface [108].

One of the major parameters affecting the surface energy and consequently the wettability of particles is “zeta potential.” When a solid surface and a liquid surface come into contact with one another, exactly on the solid-liquid interface surface, an electrical double layer is formed. This double layer is composed of two regions: (1) an inner part, which includes the ions that not only are tightly bound together but also are tightly bound to the surface, and (2) an outer part where the ions come to an electrostatic balance. As the distance from the interface surface is increased, the potential decreases. This gradual decline continues until a sufficient distance (inside the bulk solution) that the potential reaches a conventional value of zero. The double layer and the decay of potential may be seen in figure 17 and 18. Zeta potential is defined as the potential value at the surface of shear. Zeta potential is a function of surface charge and reflects the effective charge of the particle. Therefore, zeta potential represents the electrostatic repulsion between the charges. When a layer of micro-molecules is adsorbed on the solid surface, then the shear plane is shifted further from the surface and the zeta potential is changed [120].

The investigations of some researchers show that aggregates which impart a high pH value to the contact water and/or have a high zeta potential, have a high propensity and potential for stripping [108] [113].


Particle surface
Stern plane
Surface of shear
Diffuse layer
Stern layer
Ψo
Ψδ
ζ
0
Potential
Zeta
Potential
(ζ)
δ
1/κ
Distance
Stern
layer
Diffuse
layer
Electrical double layer

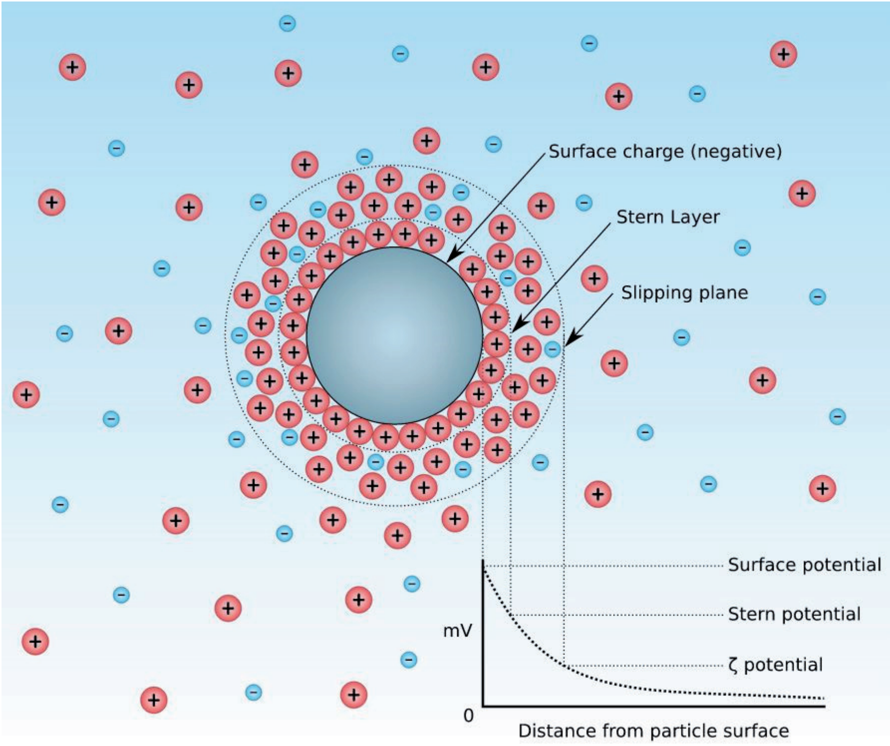


Figure 17 : Distribution of charges at the aggregate-bitumen contact surface, around an aggregate particle and zeta potential [112] [120] [121]

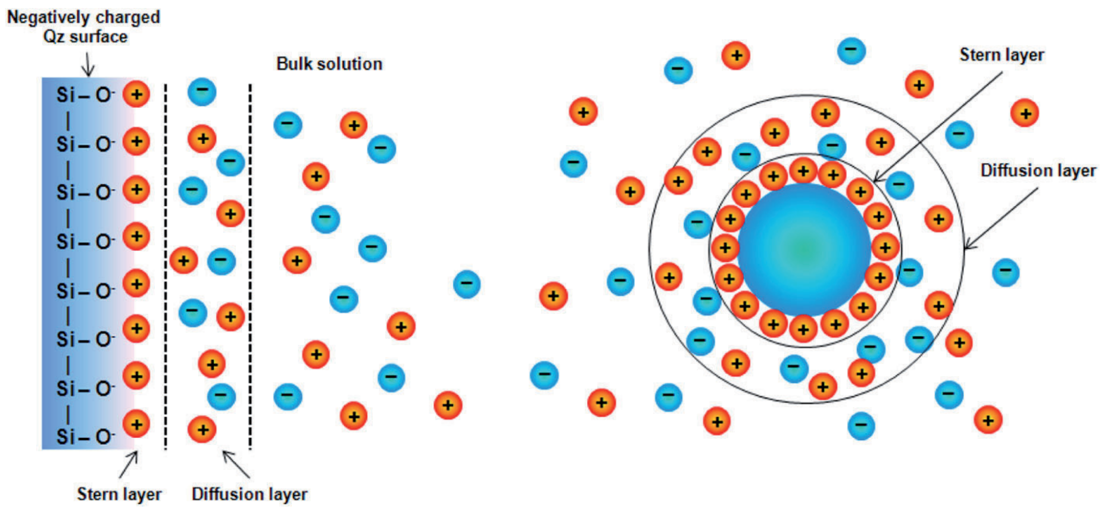


Figure 18 : Electrical double layer around quartz surface (left) and a charged particle (right). Si=Silicon and the Stern-layer refers to the layer of ions closest to the surface [122]

According to the other researches, the intensity of repulsion developed between bitumen and aggregate surfaces depends also on surface charges of both bitumen and aggregate. Zeta potential is used in order to measure the aggregate surface charge. Based on the measurements, a general trend was found out. The trend revealed that aggregates with relatively high surface potential in water (higher zeta potential) have a higher debonding potential and more susceptible to stripping (figure 19) [108] [123].

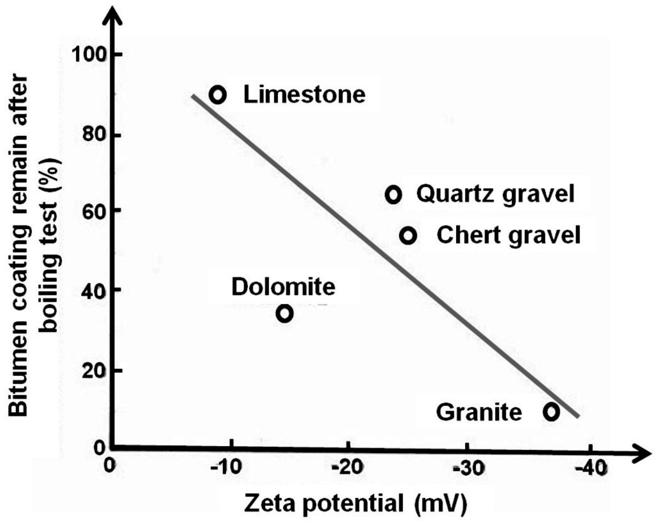


Figure 19 : Aggregate surface potential vs. stripping propensity determined by boiling water test [123]

As a result of this theory, every single aggregate grain has its particular surface charge which is mainly a function of its chemical components. Figure 20 shows a classification of aggregates based on aggregates surface charge.

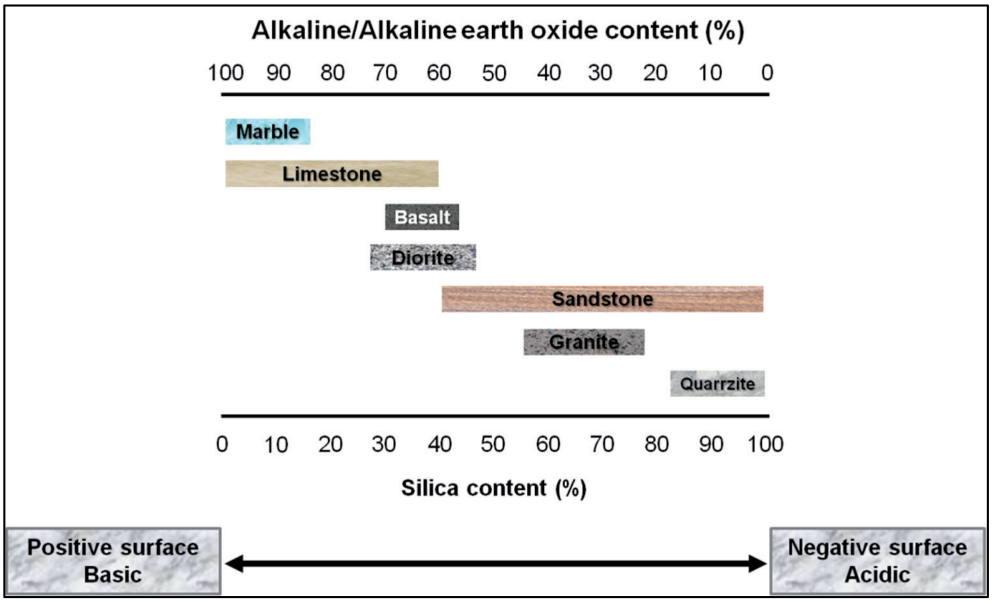


Figure 20 : Aggregates classification based on their silica content, alkali content and surface electrical charges [112] [124]

3.2.2.1.4 Thermodynamic adhesion theory

The *thermodynamic adhesion theory* is broadly applied in adhesion science. It is based upon the interfacial or boundary energy with particular considerations on the polarity of molecules. Since polar liquids are better attracted to aggregates surface than the not polar liquids, it is believed that this characteristic leads to the fact that water accelerates the separation of bitumen from aggregates´ surface. This theory suggests that, adhesion is a result of intermolecular forces related to the surface free energy and is characterized by various factors such as wettability or wetting, spreading and contact angle between the liquid´s drop and solid surface. In fact, this theory considers the wetting, diffusion, and detachment of bitumen from aggregates surface as a thermodynamic process [104] [112] [125] [110]. The thermodynamic equilibrium between the three-phase system of liquid, solid and water is studied by three different models, which are briefly discussed as below:

3.2.2.1.4.1 Young´s model

The wetting or wettability of a solid surface by a fluid/liquid is recognized by the contact angle between the solid-liquid interface and the liquid-vapor interface through “Young´s equation." The hydrophilicity (water loving) and hydrophobicity (water hating) of a surface is also determined through the contact angle.

As an example for a super hydrophobic surface, the contact angle of a drop of water is greater than 150°, which brings no contact between the drop and the substance surface [126].

Surface properties such as cleanliness and roughness also affect the contact angle (will be discussed later). Figures 21 to 23 show different situations of a drop of liquid over a solid surface.

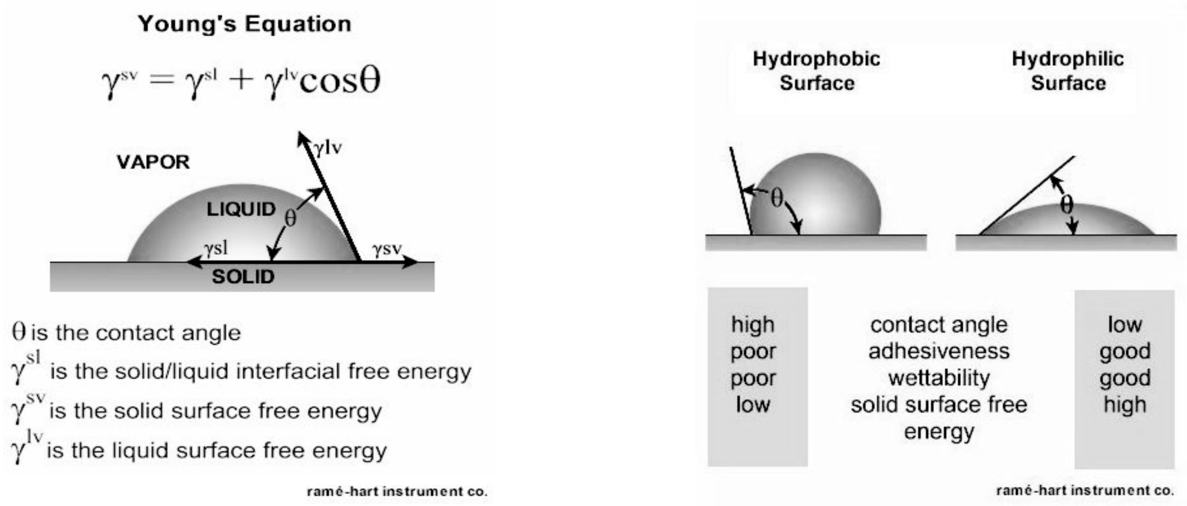


Figure 21: Contact angle and the Young´s equation for a drop of liquid in contact with a solid surface [127]

Table 4 : Solid surface as a function of contact angle [128]

Contact angle	Degree of wetting	Solid surface type	Strength of :	
			Solid/liquid interactions	Liquid/liquid interactions
θ = 0	Perfect wetting	Hydrophile (attracted to water)	Strong	Weak
0° < θ < 90°	High wettability		Strong	Strong
			Weak	Weak
90° < θ <180°	Low wettability	Hydrophobe (repelled from water)	Weak	Strong
θ = 180°	Perfectly non-wetting		Weak	Strong

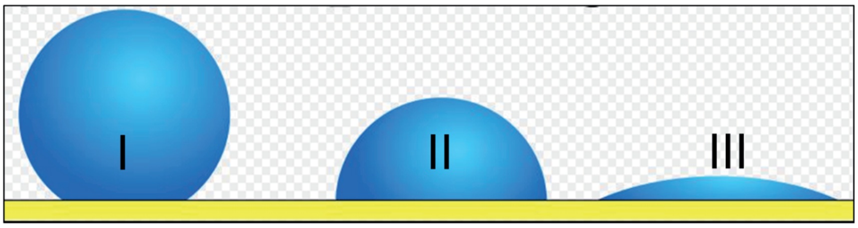


Figure 22 : Different wetting of a surface by a liquid: (I) very low wetting/large contact angle/low surface energy/hydrophobe, (II) medium wetting, and (III) high wetting/small contact angle/high surface energy/hydrophile [128]

The contamination of the interface area between the liquid and the solid also has impact over the wettability of the solid. Specially in case of organic contaminants, it increases the contact angle and leads to a low wetting on a hydrophile surface [127].

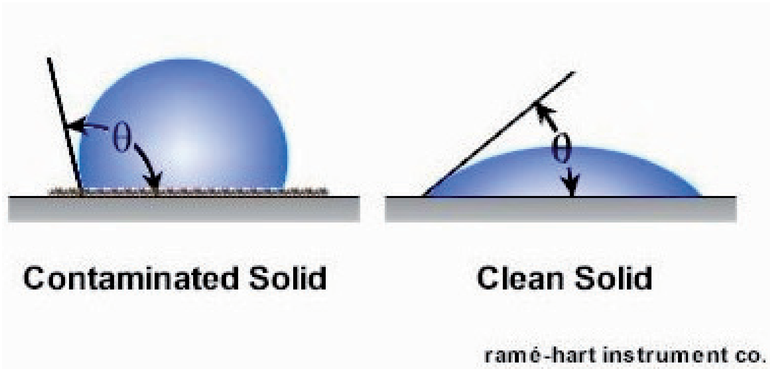


Figure 23 : Effect of cleanliness of the interface area (between solid and liquid drop) on the wettability [127]

The young´s equation is applied for ideally smooth, rigid and flat surfaces, but when the surface is not ideal and has roughness or micro/nano textures (namely SO-surfaces), then the surface roughness leads to a deviation in contact angle from the value predicted by young´s equation and enhances the wettability (e.g. a chemically hydrophilic surface becomes more hydrophilic when surface roughness is introduced to the system and vice-versa).

There are two important models regarding contact angle and the wetting process of non ideal micro structured surfaces: Wenzel´s model and Cassie-Baxter model. These models are briefly mentioned below [128] [129] [130] [131] [132] [133] [134] [135] [136] [137] [138].

3.2.2.1.4.2 Wenzel´s model

Wenzel´s model states that whatever trend a rough surface has, when water is penetrated into the roughness, this trend is enhanced. Based on Wenzel´s theory, the contact angle of a wetting liquid (θ<90°) will become smaller when the solid is roughened (a hydrophilic surface will become more hydrophilic) and the contact angle of a non-wetting liquid (θ>90°) will be larger when the roughness of a surface increases (hydrophobic surface will become more hydrophobic). In other words the roughness leads to an amplification of the wetting properties of a (smooth) material if a drop of liquid wets the surface. There are two assumptions by this model: firstly this model actually is related to the homogenous wetting regime (liquid fills the roughness grooves on the homogeneous surface) which means it is regarded to be used for chemically homogenous rough surfaces and secondly, the structures of the surface are smaller than the liquid droplet. In this model the drops are penetrated and engulfed the surface corrugations, cuts and grooves. This model predicts that either the hydrophilic or the hydrophobic character of a smooth surface is amplified by making it rugged.

3.2.2.1.4.3 Cassie-Baxter model

Cassie-Baxter model is related to heterogeneous wetting regimes (heterogeneous surfaces with different patches), which means more materials are involved (actually when the liquid droplet does not penetrate into the groves then the Wenzel´s model does not apply and the Cassie-Baxter model is used). In this case, the surface is rougher and the roughness grooves are larger and have more height. The drop is suspended upon the top of the asperities and roughness feature and the air bubbles (gas phase) are trapped underneath. The trapped air may increase the contact angle leading to a super-hydrophobic surface. This model is interesting since the air bubbles/layer trapped between the solid surface and the liquid phase, could act the role of a lubricant and has the ability to induce a large slippage of the fluid (slippage might not be perfect as it shall compete with the friction applied by the roughness).This phase is named as the “filling transition” of the cavities and micro channels (which leads to loss of adhesion between bitumen-aggregate surface). Filling transition is a function of geometry, contact angle, slip properties and slip length of the surface. Filling process is favored by the sharp corners inside the micro-structures. This model is more regarded to hydrophobic surfaces and higher degree of roughness.

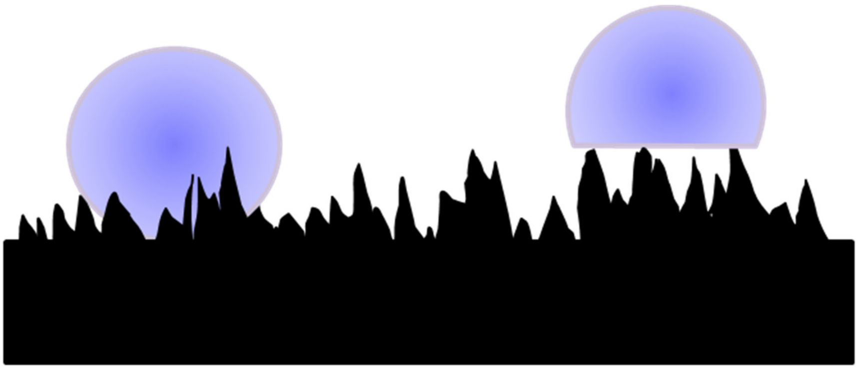


Figure 24 : Contact angle and wetting state on a rough surface, (a) Winzel´s model and, (b) Cassie-Baxter model

3.2.2.1.4.4 The effect of pressure and Temperature on contact angle and wettability

Wettability is the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids [139]. In other words, it is the ability of a fluid phase to preferentially wet a solid surface in the presence of a second immiscible phase [140]. Two main parameters that influnce the wettability and correspondingly the contact angle are temperature and pressure. Detailed studies have been carried out on the effect of temperature and pressure on contact angle. As an example for hydrophobic surfaces such as quartz, the increase in temperature and pressure may lead to a decrease in contact angle between bitumen and water. No difference if the bitumen is a drop and water is the bulk phase or vice-versa. Also doesn’t matter if the surface is first exposed to one of the fluids (bitumen or water) and then a drop of the other fluid is placed over it or if first the drop is placed on the surface and then the surface is exposed to the other fluid. In any case, a rise in pressure and temperature result in a decrease in contact angle (system goes toward more water-wetness properties). In fact, in case of a hydrophobic surface like quartz which is an oil-loving substance, increase in temperature and pressure generally leads the whole system to be more water-wet than oil-wet, which means quartz surface shows more water-wet affinity. In reality the effect of temperature is more than pressure, it means in constant pressures, by rise in temperature the contact angle decreases and thus the surface shows more water affinity. The size of the water drops is also a decisive factor. The smaller the water drops, the easier it is for the water drop to spread over quartz surface. It means even in case of a hydrophobic surface, the surface is more water wet when the water drops are smaller in size [141].

A very important notification is that under temperature and pressure rise, the order of surface exposure influences the wettability characteristics of the surface. It means when the surface is first exposed to water then it will gain more water-wet properties and it is simply because the polar molecules of water are absorbed by the surface molecules [141].

As a result of above discussion regarding the contact angle formation, to understand why various surfaces and liquids generate different contact angles, the interaction between liquid-surface molecules and the liquid molecules themselves has to be studied. When a droplet places over a surface, the adhesion force (attractive force between unlike molecules) between solid surface and liquid tries to spread the drop over the surface and on the other hand the cohesion force (intermolecular attractive force between like molecules and responsible for the surface tension of a liquid) within the molecules of the liquid resist against this adhesion force and try to ball up again. They keep their drop shape and avoid contact to the surface. When the surface energy of the solid surface is more than the surface tension of the liquid droplet, then the wetting takes place [118] [129].

3.2.2.2 Separation process mechanisms (stripping mechanisms)

Again, in this field, some other mechanisms are developed within the last decades and they all try to explain the asphalt deterioration problem in a different point of view. Actually, there are two main disbonding mechanisms, specifically cohesive and adhesive, by which the bitumen/aggregate system may fail. In case, the aggregates are clean, dried and the asphalt mixture is impermeable but still a failure takes place, then it is cohesive problem. In other case which takes place mostly in the presence of water, the adhesive bonding between aggregate and bitumen is lost. In this case, the stripping of bitumen from aggregate surface will take place. The mechanisms of disbonding are as below:

3.2.2.2.1 Displacement

The *displacement mechanism* is related to the thermodynamic equilibrium of the three phase (bitumen/aggregate/water) system. It is based on a condition that the surface of aggregate is not fully covered with bitumen from the beginning. The entrance of water through bitumen-aggregate interface which is mainly due to different polarities, leads to detachment and separation of bitumen from the aggregate surface [125] [110] [109]. Binder displacement phenomenon may take place when the aggregate is not fully covered with bitumen, the binder (bitumen) has not reached its final viscosity (e.g., when raining at the time of hot asphalting) or loss of aggregate on the surface of the asphalt pavement has occurred [104].
Figure 25 shows an aggregate particle embedded in a bitumen layer in dry and wet situation. Point A is the equilibrium contact position in dry system and point B represents new intersection point in wet system. When the aggregate is in contact with water, the equilibrium point A shifts down and retracts over the surface to Point B. As it is clear in figure 25, moving from point A to point B causes the contact angle to increase. This phenomenon happens when water is introduced to bitumen/aggregate system, causing the bitumen film to retract along the surface of the aggregate because of surface energy changes [109].

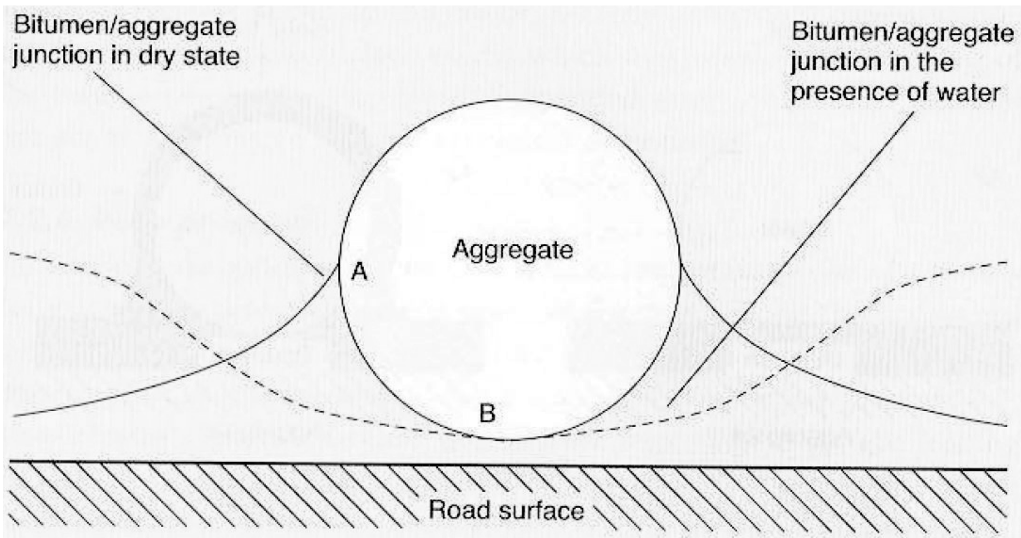


Figure 25 : Retraction of bitumen layer in the presence of water [109]

In fact, stripping by means of displacement is the result of water penetration to the bitumen-aggregate surface through a discontinuity or break in the bitumen film, which causes the removal of bitumen film from the aggregate surface. This break may have been caused by incomplete coating of the aggregate surface initially or by film rupture (where bitumen, aggregate and water are in contact with each other). This is because bitumen layer at these regions is usually thinner. On the other hand, the rupture of bitumen film takes place probably at the sharp edges and corners of angular aggregates under traffic load. The displacement of bitumen may also be from the pinholes in bitumen film. The existence of pinholes and craters in bitumen layer could be a fast result of the coating of a dusty aggregate. Stripping by means of displacement may also be explained from chemical point of view. With the passage of time, microscopic water vapor is accumulated on aggregate surface (entered from the point of disruption). The change of pH of this thin microscopic water layer changes not only the type of polar groups absorbed on aggregate surface but also the state of ionization/dissociation giving rise to opposing negatively charged electrical double layer on the aggregate and also bitumen surfaces. In order to achieve equilibrium, more water molecules are attracted to aggregate surface and this leads to the separation of bitumen layer from the mineral aggregate surface. The final result of stripping by displacement is the displacement of bitumen layer from aggregate surface because of the interfacial energy effect [142] [143] [108] [113].

3.2.2.2.2 Detachment

The *detachment or infiltration mechanism* is similar to the displacement mechanism. However the effect goes ahead and proceeds in such a way that the presence of moisture and dust on the surface of the rock, is treated as a contributing factor for infiltration of bitumen by water on the interface surface. As a result of this mechanism, the bonding or adhesion between bitumen and aggregate is disturbed. Therefore, detachment mechanism is dealing with the damage of adhesion bond between aggregate and bitumen [104] [125] [110] [111].

Based on the infiltration mechanism, the detachment happens when a thin layer of water or dust causes the separation of bitumen film from aggregate surface with no obvious break and discontinuity in the surface of bitumen layer. Thus, detachment differs from displacement in the sense that displacement involves the separation of bitumen film from aggregate surface through a break in the bitumen film, but in detachment, no obvious break is apparent. In this case although the bitumen layer encapsulates and fully covers the aggregate particle, but in the reality there is no adhesive bond between aggregate surface and bitumen. Therefore, bitumen can be easily peeled off from aggregate surface [109] [144].

This mechanism could also be explained from chemical point of view and that is: If water penetrates through bitumen film and reaches the aggregate surface, in case the conditions are so (provided) that micro-droplets are formed underneath the bitumen layer, then the pH achieved might be sufficient to ionize and dissociate the absorbed bitumen molecules [108] [113].

The thin water layer (at the interface) may come from:

(a) A sub monolayer of water, which was not dried off from the aggregate surface,

(b) Interstitial pore water, which was initially lodged into the pores but vaporized and then condensed on the aggregate surface, or

(c) Water, which permeated through the bitumen layer and reached the interface layer [113].

In order to have a better understanding of detachment mechanism, a more detailed technical explanation is provided below.

The first step to have an adhesion bonding between aggregate surface and bitumen is to have a good acceptable bond between bitumen and aggregate. Having such bond depends on the ability of bitumen to wet the aggregate surface. The wettability of an aggregate surface increases as the surface tension or free surface energy of adhesion decreases. Results from scientific researches shows that the surface tension of water is much lower than that of bitumen (asphalt). In a three-phase interface system consisting of aggregate, bitumen, and water the total surface energy tends to be minimized. In order to gain a stable thermodynamic condition with a minimum surface energy, water will wet the aggregate surface. This is because water reduces the surface energy of the system more than bitumen. Thus, it is the main reason why water film will cause the detachment of bitumen layer from aggregate surface [142] [108] [144].

From interfacial energy point of view, the effect of polarity of the molecules being present at the surface of the two phases must be under concentration. Most of the aggregates have electrically charged surfaces. Bitumen is composed of high molecular weight hydrocarbons, which present low polar activity. Therefore, the bond established between bitumen and aggregate surface is due to the relatively weak dispersion force. On the other hand water is an extremely polar molecule and is attracted to the aggregate surface by much stronger orientation force, which means it can replace the bitumen at the bitumen-aggregate interface [142] [108] [145]. Actually where stripping by detachment takes place, the bitumen layer is peeled cleanly from the aggregate surface exhibiting a complete loss of adhesion [142].

3.2.2.2.3 Pore pressure

The *pore pressure mechanism* assumes that water enters (into) the asphalt pores and openings. Because of traffic load, water is forced and pressed into the pore spaces. The high pore pressure results in detachment of bitumen from the aggregate surface. This mechanism likewise presumes that due to temperature fluctuations, water pore pressure is changed and therefore leads to adhesion loss in the interface layer and thus (ends up to) fatigue of the asphalt [125] [110] [146]. To be more precise, this type of disbonding mechanism normally takes place in poorly compacted mixtures or high void mixes. Therefore, water has the possibility to be trapped in the pore structures of HMA because of traffic compaction and may circulate freely through the interconnected voids. Moreover as the material is fully compacted and traffic loading causes densification of the asphalt mix, water may be trapped in impermeable voids that previously permitted water circulation and then the subsequent further trafficking induces and generates (high excess) water pore pressure. Because of this, micro channels are developed around the bitumen-aggregate surface interface leading to an adhesion bond loss and finally stripping occurrence.

The stresses, which are imparted to the entrapped water on behalf of repeated traffic load, will worsen the damage. The continuous buildup of pore pressure disrupts the bitumen layer from the aggregate surface and may also cause the growth of micro cracks in the asphalt mastics. The formation and development of micro-cracks in the asphalt mastics itself, under heavy repeated loading shall also be under concentration. Therefore, due to pore pressure, the stripping process may lead to cohesion or adhesion failure or even both. Researchers have shown that the damage dramatically increases as the micro-cracking progresses. The rate of this damage is exacerbated in the presence of water. This is because the development of pore pressure in micro-cracks and micro voids increases the rate of crack growth. Pore pressure progress also increases:

(a) Damages at the rock tips caused by the development of higher pressures, and

(b) Damages to asphalt mix through weakening the adhesive bond between the mastic and aggregate as well as the mastics itself [109] [142] [108] [113].

Some researchers have this idea that most of the water problems with asphalt occurs within 5% to 12% of air void content. This range is called as “pessimum” air void range, which is actually the antonym of optimum void range. Less than 5% void, is low air void and the air voids are disconnected and relatively impermeable and therefore they will not be saturated with water. Above 12% is high air void and the air voids are interconnected and the moisture may flow out under a stress gradient developed by traffic loading. Within this range (5% to 12%) is pessimum and water can enter the voids but do not have the ability to get out and escape freely and thus is subjected to pore pressure progress upon repeated loading (Figure 26) [108] [147].

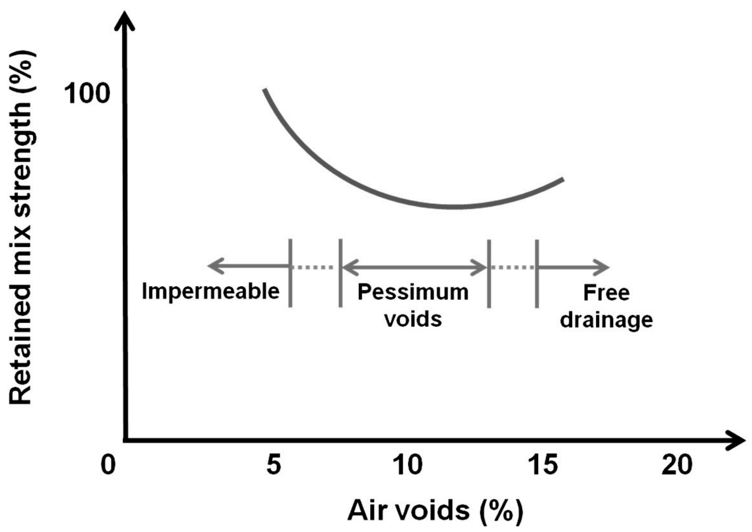


Figure 26 : Relationship between air void content and retained strength of mixtures following water conditioning and showing the region of pessimum void [147] [148]

The effect of temperature on this mechanism is negative, which means a rise in temperature acting on entrapped water expands stresses, accelerates water migration, and causes disbonding. A decrease in temperature also results in ice formation (freeze-thaw cycling) which is also destructive. This mechanism usually takes place from the bottom of asphalt layer (because it is under tension) towards the top (which leads to stripping) and the segregation is prevalent at the layer boundaries [109] [142] [108] [113].

3.2.2.2.4 Film rupture

The *film rupture mechanism,* deals with the creation of cracks in the thin bitumen layer (film) because of dynamic load effect, which results from traffic load. It causes water to enter under bitumen layer and disturb the bitumen coating. These kinds of cracks are more expected to be seen at the sharp edges and corners where the thickness of bitumen reaches its thinnest [110].

In fact, although aggregate might be fully coated with bitumen but still the film rupture may occur. Therefore, the film rupture causes the initiation of stripping due to film fissures, which happens at sharp aggregate contacts, edges or asperities. The presence of dust fine particles on the surface of aggregates (which enhances the formation of blisters and pits) can also cause film rupture. The rupture might be a consequence of construction load, operating traffic loads under service conditions or even environmental reasons such as freeze-thaw cycles. A small tiny crack or break in bitumen film, leads to water absorption (in form of moisture, vapor or liquid), penetration and spread between bitumen and aggregate interface. This causes the detachment of bitumen film from aggregate and finally results in the retraction of bitumen layer and film rupture. The rate of water penetration and detachment of bitumen is a function of bitumen viscosity, mineralogy of aggregate, nature of aggregate surface, thickness of bitumen film, the presence of fillers and other surface coatings or components such as surface active agents (surfactants) [109] [113] .

3.2.2.2.5 Hydraulic scouring

The hydraulic scouring mechanism is related to the action of the vehicle´s tires and is applicable to surface courses. This means hydraulic scouring is mostly seen on the surface of the streets (ravelling phenomenon). On the saturated pavement surfaces, tires force the water into the surface voids and then due to compression-tension cycles (water is pressed down and forced into the pavement surface voids in front of the tires and sucked away from the pavement behind the tire) disbonding of bitumen and the aggregate surface occurs. In other words, bitumen layer is stripped off from aggregate surface. The existence of dust and silt size fines and their mixture with water may act as an abrasive material and accelerate the disbonding [109] [142] [108] [113]. Osmosis and pullback have also been suggested as two possible mechanisms of scouring [149].

3.2.2.2.6 Chemical disbonding

The *chemical disbonding mechanism deals* with the formation of double layers at water-aggregate surface. As the water penetrates through the bitumen film on the aggregate surface, it causes the (aggregate´s) surface to show a negative surface charge. On the other hand, bitumen has also slightly negative charges. As a result, two negatively charged surfaces are in contact with each other and repulsion will take place. With passage of time, the amount of water attracted to the aggregate surface increases, the repulsion also enhances and finally disbonding of the bitumen film will happen [109] [150].

3.2.2.2.7 Spontaneous emulsification

The *spontaneous emulsification mechanism* is the formation of inverted emulsion of water droplets in bitumen medium. In another word, bitumen is the bulk or continuous phase and water is the discontinuous phase. The formation and penetration of such an emulsion between aggregate surface and bitumen, breaks the adhesive bonding and leads to stripping. These types of emulsions form when asphalt (consequently bitumen) is immersed in water. This process is exacerbated under traffic conditions on mixtures laden with free water. The nature of bitumen and the existence of additives have impact on the rate of emulsification. The formation of spontaneous emulsions is further aggravated by the presence of some anti-stripping products, hydrophilic calcareous minerals, some bag-house fines and emulsifiers such as clays and asphalt additives, which means the probability of formation of inverse asphalt emulsions is enhanced [142] [143] [108] [113] [149] [151] [152].

3.2.2.2.8 pH instability

The *pH instability mechanism* deals with the fact that the adhesion between asphalt and aggregate is influenced by the contact water pH value. Some researchers believe that the pH value of contact water has impact on the contact angle and the wetting properties of aggregate-bitumen interface. As an example (based on performed experiments) the interfacial tension between aggregate surface and hydrophilic surface reaches its maximum at intermediate pH (pH=9) and drops as the pH increases. As a result of various inquiries the stabilization of the pH sensitivity at aggregate-bitumen interface may minimize the potential for bond breakage, establishes strong and durable bonds and therefore reduces the stripping effect [143] [108] [113] [153] [154].

3.2.2.2.9 Environment effects

The most significant environmental factors that have substantial and considerable impacts on the resistance and durability of asphalt pavements are air, water (e.g., rain water and ground water) and temperature fluctuations (e.g., freeze-thaw cycles). In locations with moderate climate, were good quality aggregate and asphalt are available, the major contribution to deterioration of asphalt concrete is the traffic load. To have an idea about the amount of traffic load (applied) on asphalt surface, it is on record that a 32 ton truck exerts ca. 1,5 bar, a Boeing 747 imparts ca. 14 bar and a Boeing 727 applies about 11,5 bar of pressure to the asphalt pavement. When poor aggregate material and severe weather are coupled with traffic loads, then premature problems may occur. Therefore, apart from the environmental factors, the traffic load and construction techniques are also crucial in obtaining a good quality asphalt road [108] [147].

3.2.2.3 Combination of theories and mechanisms

From the above-mentioned theories and mechanisms together, it is deduced that the main reason of adhesion loss between bitumen and aggregate is the presence of water. The water source may be different; it could be internal (from the aggregate itself) or external (from rainwater). This water can be in various forms such as humidity, condense water, evaporated crystal water or capillary water. The cohesion within bitumen itself is also an important factor that may cause failure in full coverage of aggregate surface and aggregate-aggregate bonding loss.

Since no theory or mechanism explains accurately the problem of moisture damage, researchers have attempted to combine the aforementioned theories and mechanisms. Summarized reasons describing the adhesion loss of bitumen and aggregate, can be seen in table 5 [108] [113] [155].

Table 5: Proposed relationship between theories/mechanisms of adhesive bond loss and stripping mechanisms [155]

		Theories								
		Mechanical interlock			Chemical reaction			Interfacial energy		
	Proposed operating mode	P	C	P-C	P	C	P-C	P	C	P-C
Stripping mechanisms	**Detachment**	S						S	W	
	Displacement					S		S		
	Spontaneous Emulsification				S	W				
	Film rupture	S								
	Pore pressure	S								
	Hydraulic scouring	S								
	pH instability					S				S

P = Physical
C = Chemical
P-C = Physical-Chemical
S = Primary contributor
W = Secondary contributor

As an example to this table, the detachment mechanism is a result of physical aspect of mechanical interlock theory as well as the physical and chemical aspects of interfacial energy theory. Under physical aspects, the surface energy is known whereas under chemical aspects the effect of the polarity of molecules on the boundary layer is under considerations [108] [113] [155].

3.2.3 Formation of asphalt-aggregate bond and its disruption in presence of water

The four principal bonding theories mentioned above are responsible for the formation of aggregate-asphalt bond. Aggregates have different surface charges, which is mainly a function of silica content as shown in figure 20. Rocks containing carbonate calcium have positive charge and rocks with high silica content are negatively charged. Bitumen as a binder is mostly negatively charged. The selection of binder type is a function of aggregate type. For the positively charged aggregate surfaces (which are basic, such as limestone, dolomite and basalt) the “anionic” binder are best used whereas the “cationic” binders are applied for the negatively surface charged siliceous aggregates (which are acidic, such as quartz, granite and sandstone) [156]. This is why it was mentioned in upper sections that because bitumen is mostly negatively charged, it makes better bonding with basic aggregate surfaces.

When natural rock is crushed to produce aggregates, the chemical bonds are broken. Therefore, aggregate surfaces are extremely polar and active. On the other hand, bitumen is non-polar, while water is polar. Thus in the presence of water, water molecules establish a bonding with aggregate surface as fast as possible to establish an equilibrium state. As a result of the bonding, a thin layer of water is formed between bitumen film and aggregate surface [112].

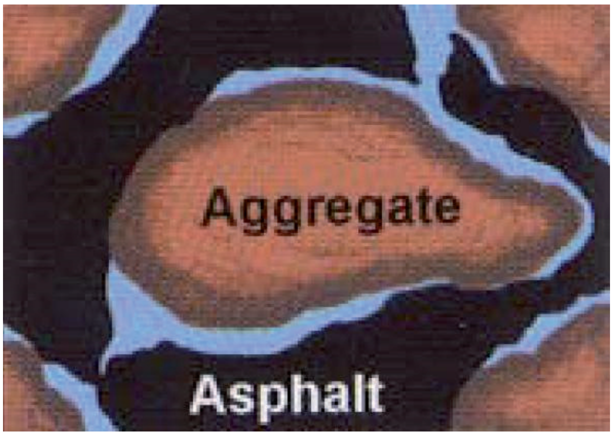


Figure 27 : Thin layer of water entering (between) the aggregate-bitumen interface [157]

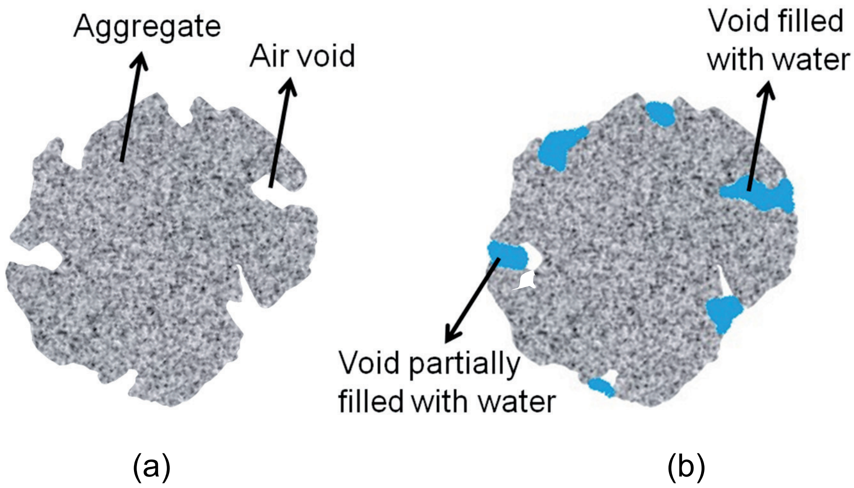


Figure 28 : Aggregate in (a) dry and (b) in wet situations [158]

Then water starts to break out the bonding between the binder-aggregate surface. In the next stage it begins to fill out the pores, air voids and cracks (Figure 27 and 28). This phenomenon leads to the creation of various asphalt quality problems such as stripping, raveling, rutting, bleeding, corrugation and shoving, pot hole and (crocodile) cracking which have been the topic of many studies till now.

Among all numerous reasons leading to asphalt quality problems, water plays an important role. Actually water has numerous harmful impacts on asphalt quality and its useful life, which are known under the term “moisture damage”. Moisture damage results in loss of strength and durability of asphalt pavements [159] .

Generally, the enterance of water through the street pavements could take place by one of the following actions [112]:

I. Permeation

In this case the rain-snow water is penetrated from the top to the down through the different asphalt layers.

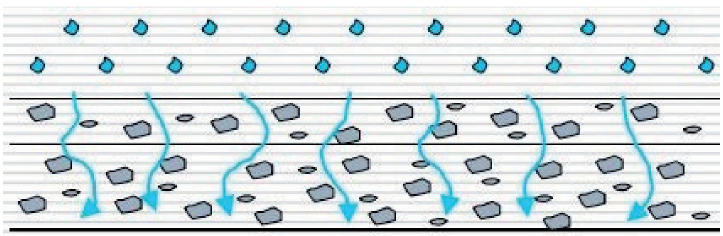


Figure 29 : Permeation of water through asphalt layers [112]

II. Capillary action

This causes water to peneterate (through the cracks) from the bottom to the top of the asphalt pavement surface. In asphalt industry it is called “water bleeding” and “pumping”.

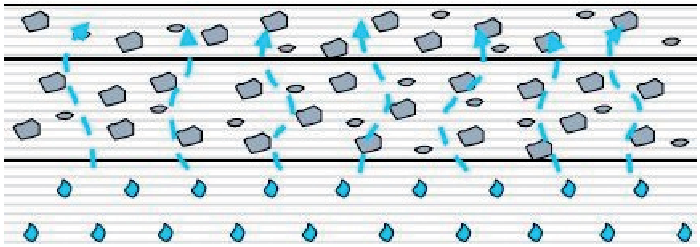


Figure 30 : Penetration of water toward asphalt surface by means of capillary action [112]

Figure 31 : Water bleeding and pumping from bottom layers to top of the pavement [160]

III. Vapour condensation

Water vapor enters the asphalt mix and begins to condense, resulting in the generation of water droplets within the asphalt mix.

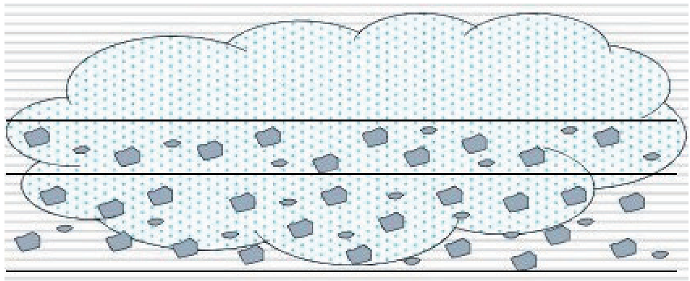


Figure 32 : Condensation of vapor in the asphalt mix [112]

IV. Traffic load

Traffic load pushes water to flow inside the contact area between bitumen and aggregate surface which leads to aggregate-bitumen bond disruptpion by action of freeze-thaw cycles.

Apart from all the different types of ways described above which leads to asphalt quality problem, a fifth way which is the main focus of this research project is discussed below:

V. Evaporation of aggregate water

Water exists in different forms such as humidity, moisture, crystal water, bound water, molecular layer water, capillary water, pore water, etc. The aggregate water which could be any kind of water such as listed above, evaporates under increased temperature and pressure situations. This evaporation exerts pressure from the inside of the aggregate toward the outside (through capillary action and pore pressure). Therefore it leads to either the formation of a thin layer of water between the aggregate-bitumen surface or causes the thin bitumen layer to be disturbed (due to the outward vapor pressure) by producing tiny small holes and craters through it (bitumen layer). The formation of microscopic holes results in the enterance of external water to the bitumen-aggregate contact area. Water evaporation may also result in both of above mentioned phenomena simultaneously (thin water layer formation and bitumen layer disturbance by means of vapor pressure).

3.2.4 Distribution of charges in aggregate-bitumen-water system

As explained earlier, aggregates gain different charges in the presence of water. Siliceous rocks acquire negative charge density on their surface when immersed in water and calcareous rocks have positive charges. In the case of our own research where the rock is basalt-andesite, aggregate surface charge is positive.

Basalt is a mafic silicate mineral rock, which contains less than 52% of SiO_2 and rich in iron (Fe) and magnesium (Mg). When it is in form of a bulk rock, then there is equilibrium between the charges. When it is crushed to form different size fractions of aggregates then the electrostatic bonds are broken and unsatisfied charges of Mg and Fe ions are generated on the fresh new formed surfaces. The following reaction reveals the fracturing process of a basaltic rock mass with the subsequent generation of infinite unsatisfied surface charges.

In case of fresh iron (iron II) the reactions are:

$$\text{Agg — Fe — Mg — Agg} \rightarrow (\text{Agg — Fe}^{+}) + (\text{Agg — Mg}^{+})$$

Alternatively, in case of iron III (oxidized iron):

$$\text{Agg — Fe — Mg — Agg} \rightarrow (\text{Agg — Fe}^{+2}) + (\text{Agg — Mg}^{+})$$

In the aforementioned reactions, “Agg” recalls the aggregate and the “—“ shows the intermolecular bonds, Fe^{+} or Mg^{+} points out to this fact that the iron or magnesium has a hand free and would like to integrate into a chemical bond. When aggregate is in contact with water or water vapor, since water is an extremely polar molecule and the surface of aggregate is also polar, they (water molecules) try to bond with aggregate surface and satisfy aggregate broken bond. The following hydration reactions will take place:

For iron II:

$$(\text{Agg—Fe}^{+}) + (\text{Agg—Mg}^{+}) + 2H_2O \rightarrow (\text{Agg—Fe—OH}) + (\text{Agg—Mg—OH}) + 2H^{+}$$

Moreover, for iron III:

$$(\text{Agg—Fe}^{+2}) + (\text{Agg—Mg}^{+}) + 3H_2O \rightarrow \left(\text{Agg—Fe}\begin{array}{l}\diagup\,\text{OH}\\ \diagdown\,\text{OH}\end{array}\right) + (\text{Agg—Mg—OH}) + 3H^{+}$$

As shown above, the unsatisfied iron ions may either absorb one hydroxyl group (OH-group) and form Fe(OH) or two hydroxyl groups and form $Fe(OH)_2$. The Magnesium ions are satisfied by absorbing one hydroxyl group to yield Mg(OH) molecules.
It does not matter what type of surface charge exist on the surface after fracturing takes place, the final structure of the charges is represented by the right hand side of the above mentioned reactions. In the presence of water, this structure is dissociated in order to form an electro-positive charge on the surface of the basaltic rocks.

For iron II : $\text{Agg Fe OH} \leftrightarrow \text{Agg Fe}^{+} + \text{OH}^{-}$

For iron III : $\text{Agg Fe (OH)}_2 \leftrightarrow \text{Agg Fe}^{+} + 2\text{OH}^{-}$

And for magnesium $\text{Agg Mg OH} \leftrightarrow \text{Agg Mg}^{+} + \text{OH}^{-}$

In all cases, the surface will have a positive charge and the OH^{-} as an anionic ion is released in the media or in the aqueous solution.
Supposing that our basaltic andesite rock consists of higher content of magnesium (mainly in magnesium carbonate phase) rather than iron, then the following reactions may also take place.
The fracturing reaction process will be:

$$\text{Agg — Mg — CO}_3\text{ — Mg — Agg} \rightarrow (\text{Agg — Mg}^{+}) + (\text{Agg — Mg}^{+}\text{ — CO}_3^{-})$$

Hydration reaction when in contact with water:

$$(\text{Agg — Mg}^{+}) + (\text{Agg — Mg — CO}_3^{-}) + \text{H}_2\text{O} \rightarrow (\text{Agg — MgOH})+(\text{Agg — Mg — HCO}_3)$$

The unsatisfied magnesium creates a bond with the OH-group and forms MgOH. The other section of the right hand side will dissociate in presence of water and creates an electro-positive charge on the surface of the rock (basalt-andesite).

$$(\text{Agg — Mg — HCO}_3) \rightarrow (\text{Agg — Mg}^{+}) + (\text{HCO}_3^{-})$$

Therefore, in any case, the surface charge of the basaltic-andesite rocks tends toward positive. Basalt is a basic igneous rock (see also figure 20) thus the aggregate surface in the presence of water/water vapor is alkaline. Although based on the above reactions, the release of proton or H^+ into the water will cause pH reduction, but on the other hand, as time progresses different compounds (which contain alkaline and earth alkaline e.g., sodium, potassium, calcium, magnesium) on the aggregate surface are hydrolyzed causing an increase in pH [161] [143] [162]. The effect of time on pH variation for different types of aggregates is shown in figure 33.

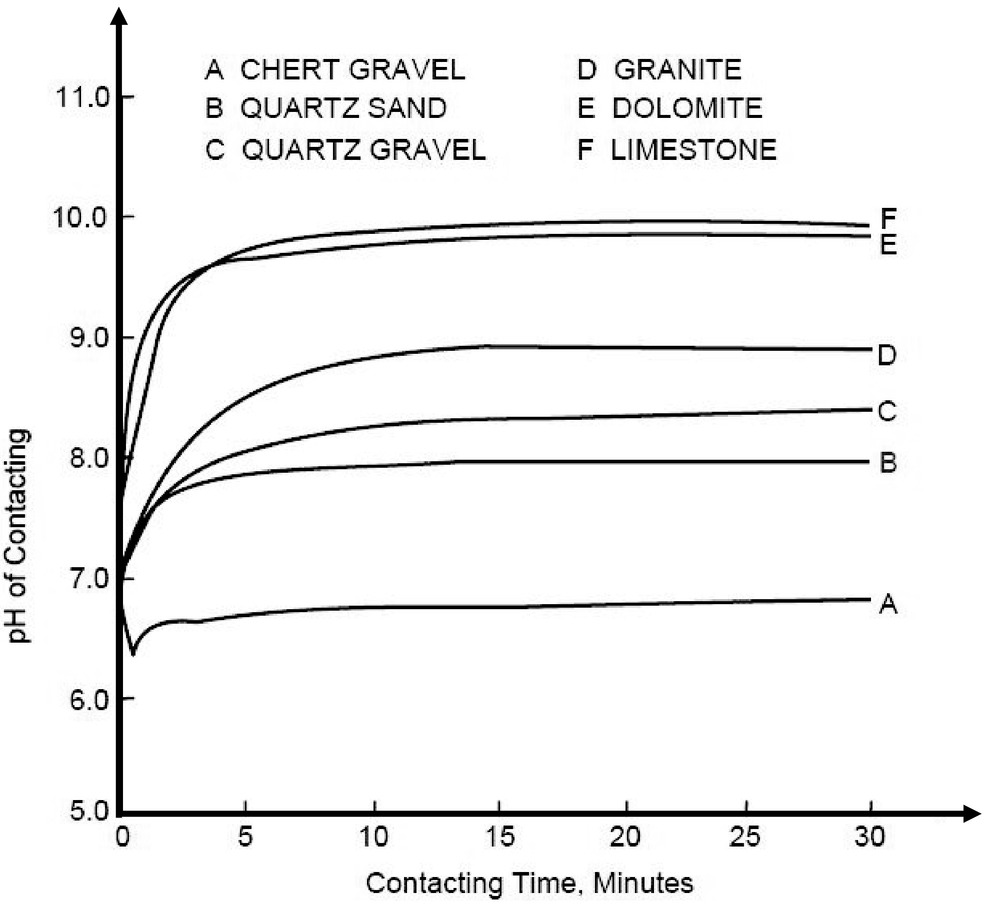


Figure 33 : Effect of time on water pH variation when various kinds of aggregates are immersed in water [123]

3.2.5 A detailed review on bitumen displacement on hydrophilic and hydrophobic surfaces

Different theories and mechanisms were considered in order to be able to understand the bitumen-aggregate adhesion and detachment system. Varius parameters such as interfacial energies, surface enregy, pH, contact angle, pH of the contact water, mineralogy of the aggregate, zeta potential and etc. play important role in either detachment or attachment process. Here a more detailed discussion is carried out in order to figure out how the bitumen is attached or loosend from an aggregate surface. Having a three phase system; aggregate, water and air in close contact to each other a combination of different parameters affect this physico-chemical connection. Change in pH and temperature of the medium has impact on the interfacial tension between bitumen and water. As the pH and temperature increases, the interfacial tension decreases. Increase in pH leads to the activation of surface-active agents such as carboxylic types, which are present at the bitumen-water interface, resulting in the decrease of interfacial tension between bitumen and water [163]. Wetting of the aggregate by water takes place if the free energy per unit area of water/aggregate interface is less than the free energy per unit area of bitumen/aggregate interface. If this happens, bitumen is released from aggregate surface, thus separation of bitumen from aggregate will take place. Water will replace the bitumen and wet the aggregate surface. pH and temperature are two principal factors which govern the interfacial energy between water and bitumen. Figure 34 shows the interfacial tension between bitumen and water in different pH and temperatures. The increase in pH and temperature leads to a decrease in interfacial tension. In fact, as the pH increases the surface-active agents (such as carboxyl-group) which are present at bitumen-water interface are activated and as a result of this activation the interfacial tension between bitumen and water decreases. An increase in temperature also causes a decrease in bitumen density [163].

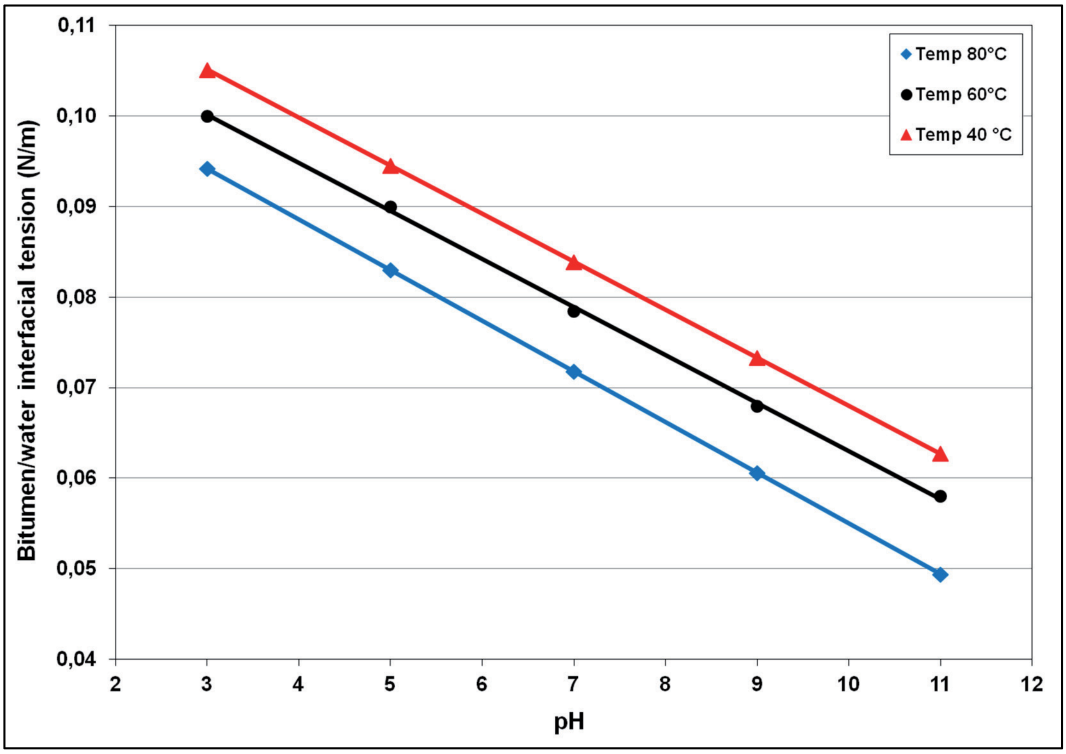
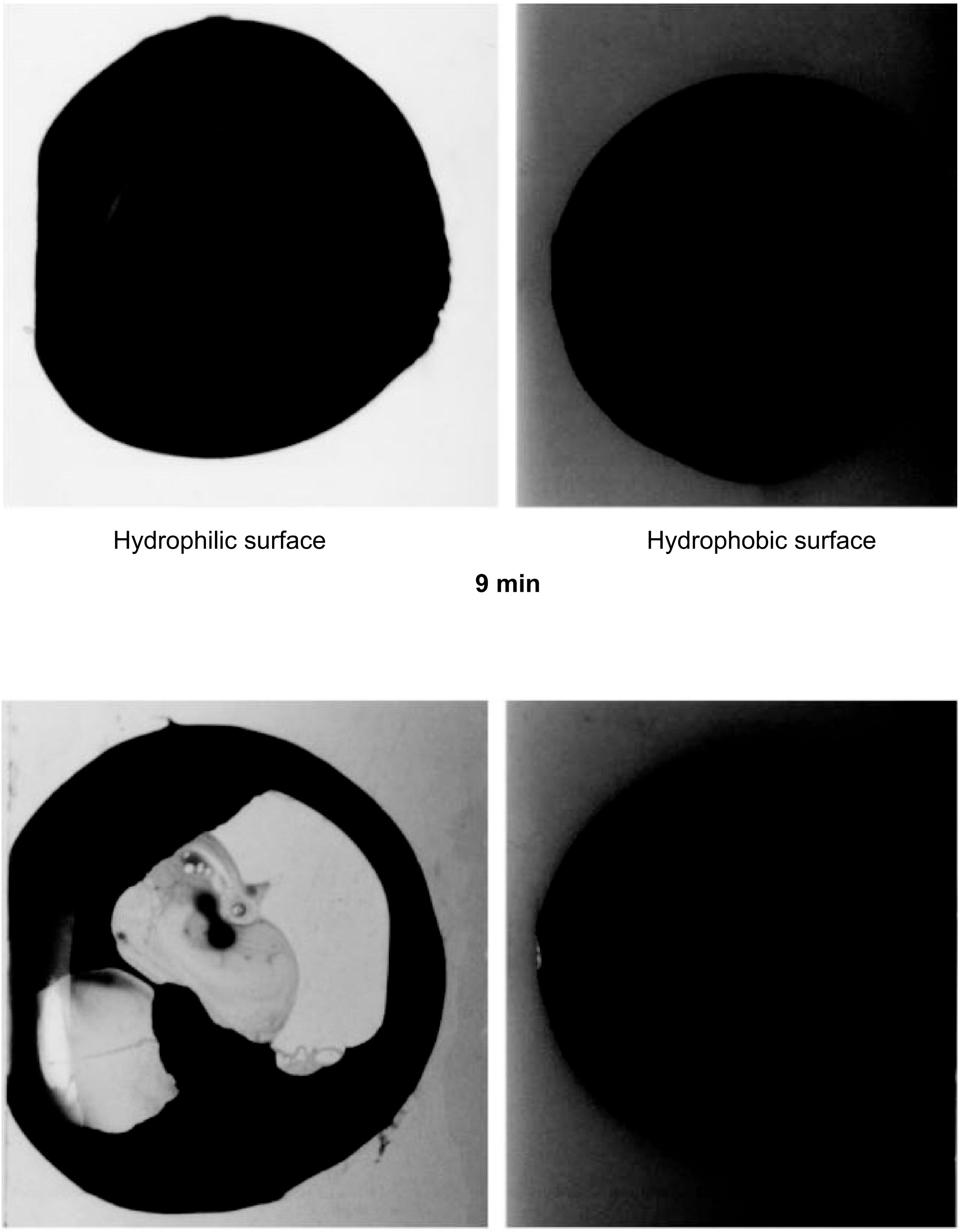


Figure 34 : Bitumen/water interfacial tension as a function of pH and temperature [163]

To have a better understanding of the bitumen film rupture mechanism from a surface in the presence of water, figure 35 is referred. In fact, in figure 35 the effect of time on bitumen rupture process is shown. First bitumen is distributed over a hydrophilic and hydrophobic surface. Afterwards water with high pH is added to the bitumen surface in form of drops. Water pH is 11 and temperature is nearly 50°C.



Hydrophilic surface Hydrophobic surface

9 min

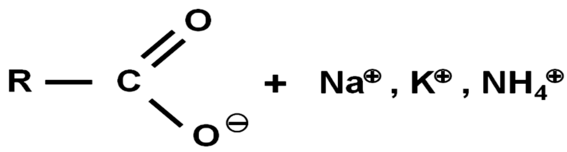
Hydrophilic surface Hydrophobic surface

16 min

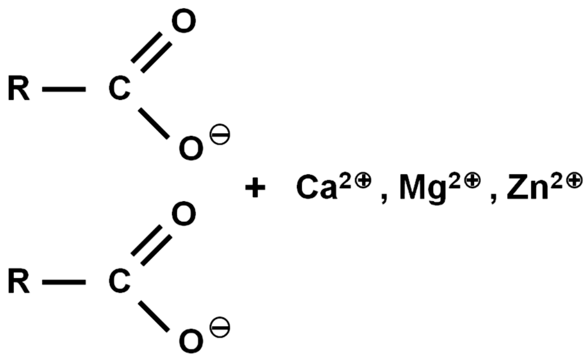
Figure 35 : Bitumen layer thinning and rupturing on different surfaces (hydrophilic and hydrophobic) as a function of time [163]

As clearly shown in figure 35, the thinning and rupturing of bitumen layer takes place on the hydrophilic surface after about 16 minutes, but bitumen film remains unchanged on the hydrophobic surface (no bitumen film rupture).

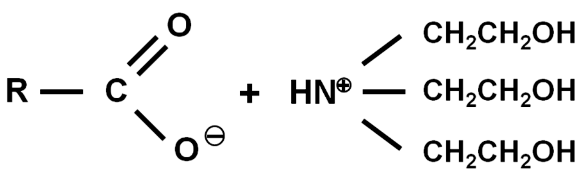
Addition of water with high pH (due to the presence of NaOH) to the bitumen-solid system, specifically over the bitumen layer, activates the alkyl carboxylic acid (which is a product of bitumen oxidation) due to absorption of Na^+ ions at the bitumen-water interface. Carboxylic acid is a kind of fatty acid, which due to its low solubility in water, is not used as surfactant, but its salt has good water affinity and is utilized as surfactant. Carboxylic acid alkali/earth alkali/ethanol amine salts are categorized as the fatty acid salt surfactants. Carboxylic acid salts are also known as soaps (surfactants and their types are discussed further on) [163].



(a)



(b)



(c)

Figure 36 : Fatty/carboxylic acid salts, (a) alkali salts, (b) earth alkali salts and, (c) ethanol amine salts (R = C7H15 – C17 H35) [164]

The activation of alkyl-carboxyl acid, which is a natural surfactant, causes the interfacial tension between bitumen and water to decrease. This decrease leads to a better flow of water drops over the bitumen surface.

The same experiments but in pH=3 has shown a different result. On a hydrophilic surface, the thinning process is much slower and the rupture of the bitumen layer does not happen. Nevertheless, in the presence of high pH water, the bitumen layer thins down and finally ruptures. However, on a hydrophobic surface nothing happens at high pHs.

If the situation is the other way around, then the hydrophilic surface is covered with water and the bitumen droplets are over it. In this case, the result is as follows. The effect of pH is in a way that the dynamic contact angle (which increases until gaining equilibrium state) of bitumen droplets on the water surface changes more rapidly at a lower pH value (pH=3) than a higher pH value (pH=11). Generally, the dynamic contact angle increases with the passage of time (figure 37). On the other hand, the equilibrium contact angle of higher pH is larger than lower pH (the equilibrium contact angle of bitumen drop increases with an increment in pH). For example the equilibrium contact angle of bitumen in pH=3 is about 107° while in pH=11 it is 170° (at 40°C) [163].

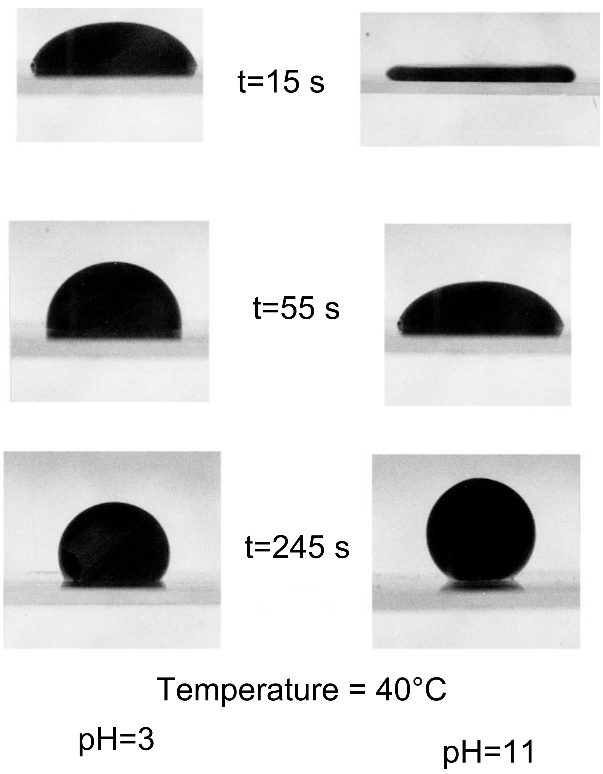


Figure 37 : Effect of pH and time on the contact angle of bitumen droplet over a hydrophilic surface (constant temperature) [163]

As shown also in figure 37, in a higher pH value the detachment of the bitumen droplet from a hydrophilic surface is easier.

Temperature has effect on the dynamic contact angle. With rise of temperature at a constant pH, the dynamic contact angle increases more rapidly. The effect of temperature on equilibrium contact angle is not that much, which means it (contact angle) shows a slight change with rise of temperature. This is mainly due to the decrease in bitumen viscosity at higher temperatures [163].

The volume of bitumen influences the dynamic contact angle but its impact on equilibrium contact angle is negligible. The lower the volume the higher the dynamic contact angle in a specific time and a constant pH. In other words, a larger bitumen sheet will require a longer time to form a bitumen droplet. Change in dynamic contact angle is inversely proportional to $V^{1/3}$ where V is the volume of bitumen [163].

Based on the explanations about the contact angles (either dynamic or equilibrium), it shall be noted that the dynamic contact angle is a function of viscosity and interfacial tension, but the equilibrium contact angle depends only on interfacial tension. The lower the equilibrium contact angle, the lower the interfacial energy, and the easier the flow of a droplet on a surface. It is important to keep in mind that in the presence of water the bitumen film on a hydrophilic surface thins down and may start to rupture, but in case of hydrophobic surface, the bitumen film is stable. The pH of water has great impact on this process; high pH value increases bitumen film thinning and rupture processes. The bitumen displacement (receding rate) on a hydrophilic surface in the presence of water is faster at low pH (dynamic contact angle of bitumen droplet is larger at low pH), but the equilibrium contact angle of bitumen droplet in the presence of water is larger at a high pH. In other words at higher pH values, the bitumen droplet is detached easier from a hydrophilic surface [163].

3.2.6 Effect of aggregate on moisture damage in asphalt concrete

A general hypothesis is that acidic aggregates are hydrophobic while basic aggregates are hydrophilic. Based on this knowledge, theoretically the stripping problem may be avoided but in fact there are many noticeable exceptions There exist actually only a few kind of aggregates which resist the stripping effect in the presence of water [108] [144].

Based on investigations, the main parameters that have impact on the bitumen-aggregate bond are surface texture, bitumen penetration into cracks and pores of aggregates, angularity of aggregates, aging of the asphalt due to environmental effects, absorbed coating on the surface of aggregates, and nature of dry/wet aggregates [142].

Regarding the effect of aggregate characteristics, some researchers believe that the following actions can enhance aggregate-bitumen bond [108] [142] [149] [165]:

(a) *Preheating of aggregates:* aggregates normally contain a thin layer of free water on their surface as well as adsorbed water in form of humidity. Heating aggregates under such a condition that the free water vapor and the outermost adsorbed water molecules are removed, may have further positive effects. It will decrease the interfacial tension of bitumen when it comes into contact with the hot aggregate surface, leading to a better wettability of aggregate by bitumen and reducing the stripping potential. Preheating may also reduce the bitumen viscosity resulting in a better penetration of bitumen into the aggregate surface and finally promoting a stronger physical bond between the aggregate and the bitumen. Therefore, the bond between the bitumen and aggregate surface is much stronger if the bitumen is applied on a hot aggregate surface than if it is applied on cold aggregate surfaces.

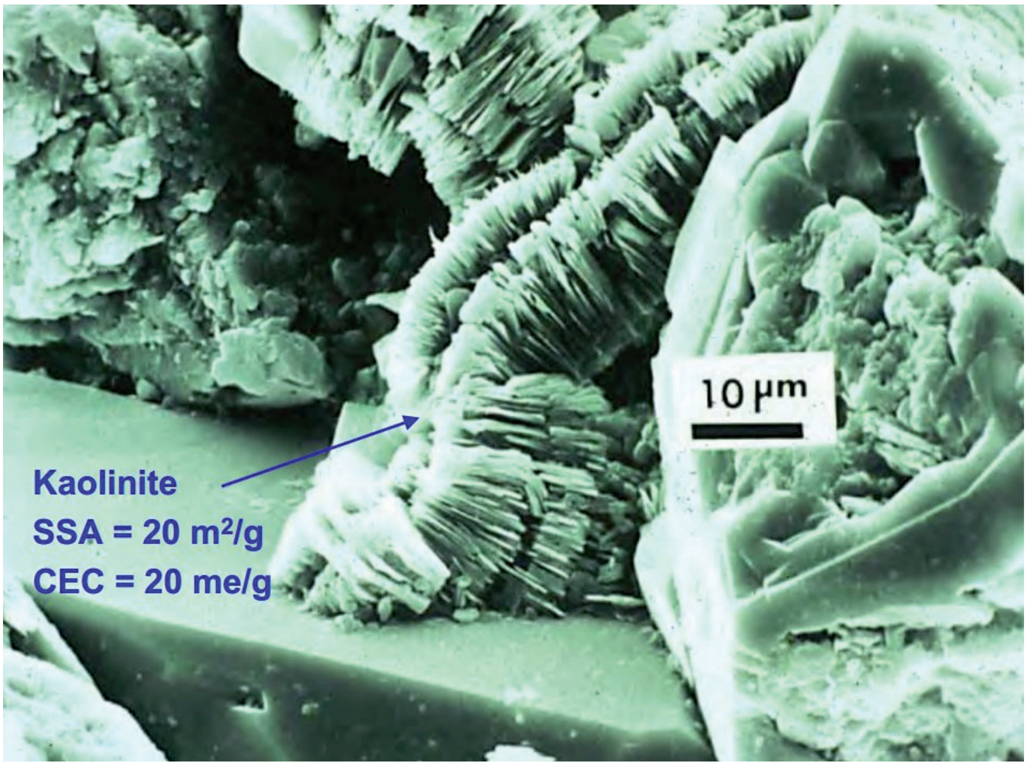
(b) *Weathering the aggregates*: by weathering process, the adsorbed water layer on aggregate surface is replaced by organic contaminants (such as organic fatty acids) from the air. This means aggregate surface will gain hydrophobic characteristics and therefore the bitumen-aggregate bonding is enhanced. It leads to a reduction in stripping coefficient. For example aggregates stored in a refinery have shown more resistance to stripping than the freshly crushed aggregates. The stored aggregates have probably adsorbed oil from the air.

(c) *Removing the aggregate coatings:* the coating material may be from dust or dirt. When the aggregate is coated with dust, it means it is coated with materials smaller than 75 µm, which leads to an interruption of bitumen-aggregate bond. The existence of a dust coating on an aggregate surface (which causes air trap) benefits the stripping process by preventing the intimate contact between the bitumen and aggregate surface, through the formation of channels in which water may penetrate and flow in. A solution to this problem could be, washing the fresh crushed aggregates in order to remove the dust particles from their surface.

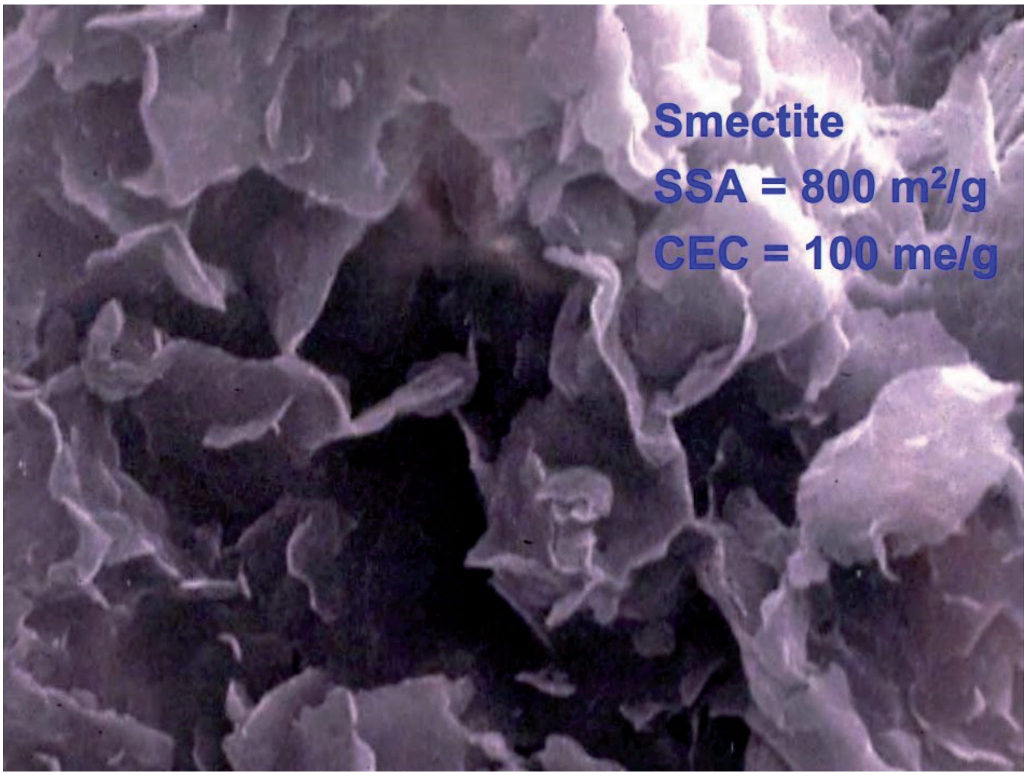
It shall be taken to account that the material type of dirt is also important. In the asphalt industry, when aggregates are coated with dirt, then it means most probably it is coated with clay minerals, and the main problems regarding the clay minerals as discussed before are [166]:

- ✓ High surface are (the ability to absorb endless water)
- ✓ Negative surface charges
- ✓ Affinity to water

Figure 38 shows the structural view of kaolinite and smectite. As it is presented, kaolinite has a specific surface area (SSA) of 20 m^2/g while for smectite is 800 m^2/g. On the other hand, the cation exchange capacity (CEC) of kaolinite is 20 me/g while for smectite is 100 me/g. These numbers reveal how destructive the presence of clay mineral groups on the surface of an aggregate could be.



(a)



(b)

Figure 38 : Specific surface area and cation exchange capacity of (a) kaolinite and, (b) smectite [166]

3.2.7 Increasing the asphalt quality through enhancing the adhesion of bitumen-aggregate bond and minimizing the rupture of adhesive bond at bitumen-aggregate interface

Despite all diverse approaches for scientific justifications and reasons for the adhesion problem (which has resulted in some developments in optimization approaches, such as the use of additives and reacting agents as bonding enhancer from which “lime stone” and “calcium hydrate” is being used increasingly in recent years), the problem has not been solved in a satisfactory way. In spite of the high costs and efforts for preparation and provision of a proper binding agent, the quality of asphalt still suffers major setbacks.

The development and application of moisture damage reducing additives and bitumen emulsions has also been the topic of many scientific papers and reports. As will be discussed in next sections, enhancement in the type of various agents is not the aim of this research, but since their usage in asphalt industry plays an important role in the improvement of asphalt quality, a brief description is presented on their functionalities.

3.2.7.1 Surfactants (surface acting agents)

The main role of a surfactant (which is a special compound) is to lower the surface tension or interfacial tension between two liquids or a liquid and a solid. They are usually organic compounds with amphiphilic properties. This means they possess both hydrophilic and hydrophobic characteristics. They are constructed from a hydrophilic groups (their head) and hydrophobic groups (their tail), thus a surfactant material contains both water-soluble and oil soluble (water insoluble) parts. They diffuse in interface layer between solid surface (aggregate surface) and oil (bitumen) or between oil and water or air and water. The hydrophilic head (water soluble) orients itself toward water phase while the hydrophobic tail (water insoluble) is directed to the oil phase (extend itself out of the water phase) [167] .

Wetting agents, anti-stripping agents, emulsifiers, dispersers, and detergents are all grouped as surfactants and all of them try to reduce the interfacial tension between oil/water or air/water and enable the mixing and wetting process.

When the surfactants are in a bulk aqueous phase, they form aggregates known as micelles (micelles are an aggregation of surfactant molecules that are dispersed in a liquid colloid), where the hydrophobic tail constructs the core of the aggregate, and the hydrophilic head is in contact with the surrounding liquid. By this action (adsorbing at the liquid-air interface), they try to reduce the surface tension of water [167] [168].

The tail of the most surfactants is similar and composed of hydrocarbon chain. The surfactants are mainly classified upon their polar head group. They are categorized into non-ionic and ionic groups. In non-ionic groups, the head carries no charge, whereas in ionic groups the head caries a net charge. If the charge is negative it is anionic surfactant, in case of positive charge it is named cationic and if the surfactant contains a head with two opposite charges it is named amphoteric or zwitterionic (dipolar ion) surfactant as shown in figure 39 [167].

In asphalt industry, the ionic surfactants are mostly used. In this case, the counter-ion part may be [167]:

(a) Monatomic or metallic

- ✓ Anions: halides; chlorides (CL^-), bromide (Br^-), iodide (I^-)

- ✓ Cations: metals; alkali metals, alkali earth metals, transition metals

(b) Polyatomic or organic

- ✓ Anions: methyl sulfate, tosyls, trifluoromethanesulfonates
- ✓ Cations: ammonium, pyridinium, triethanolamine (TEA)

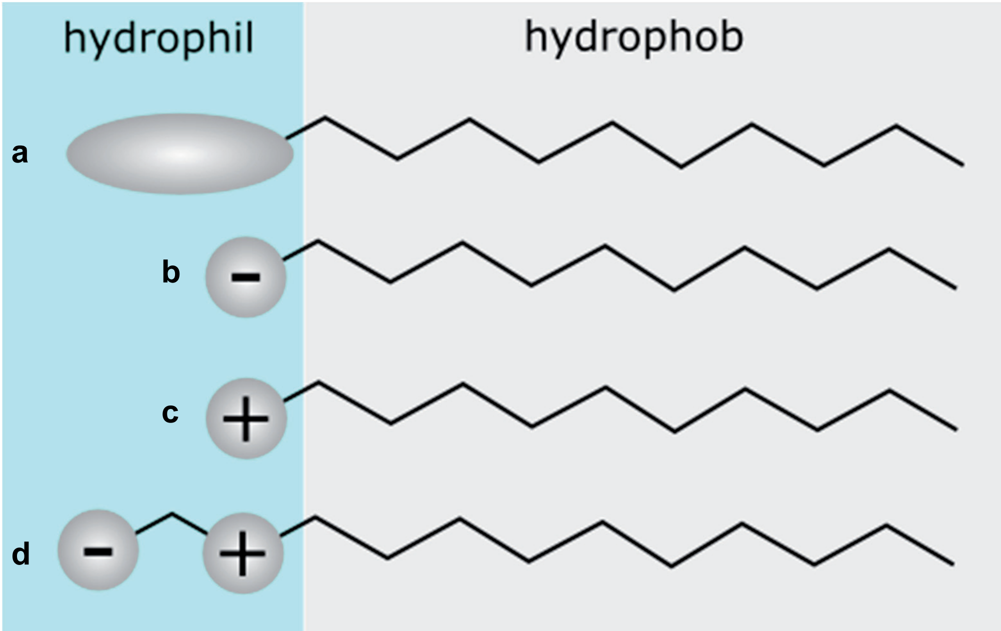


Figure 39 : Surfactant classification upon the charge of their head; (a) nonionic, (b) anionic, (c) cationic and, (d) amphoteric [167]

To have a better view of the structure of surfactants and micelles, it is referred to figures 40 to 43. Figure 40 presents the building block of a surfactant. As it is clearly shown, part (a) depicts a micelle in oil medium (water in oil), the tail of the surfactant remains in the oil phase and the polar head orients itself inside the water droplet, forming a hydrophobic outer layer. Part (b) shows a micelle in aqueous suspension (e.g. emulsion of oil in water). In this case the oil-soluble tails of the surfactant are inside the oil droplet while the water-soluble head is in contact with water phase (as it interact more strongly with water), forming a hydrophilic outer surface.

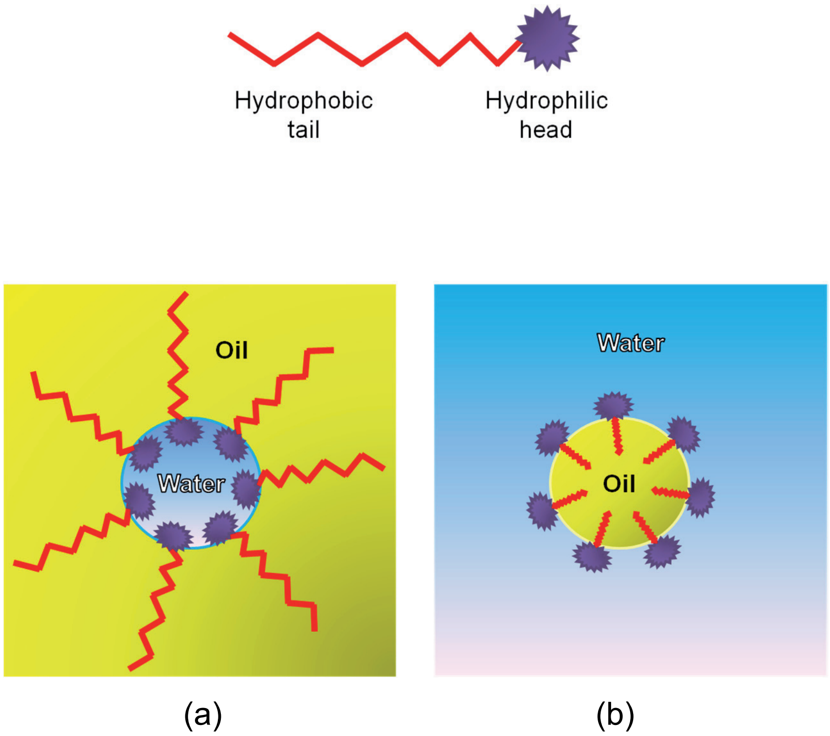


Figure 40 : Structure of a single micelle and its orientation in an an emulsion, (a) water in oil and, (b) oil in water

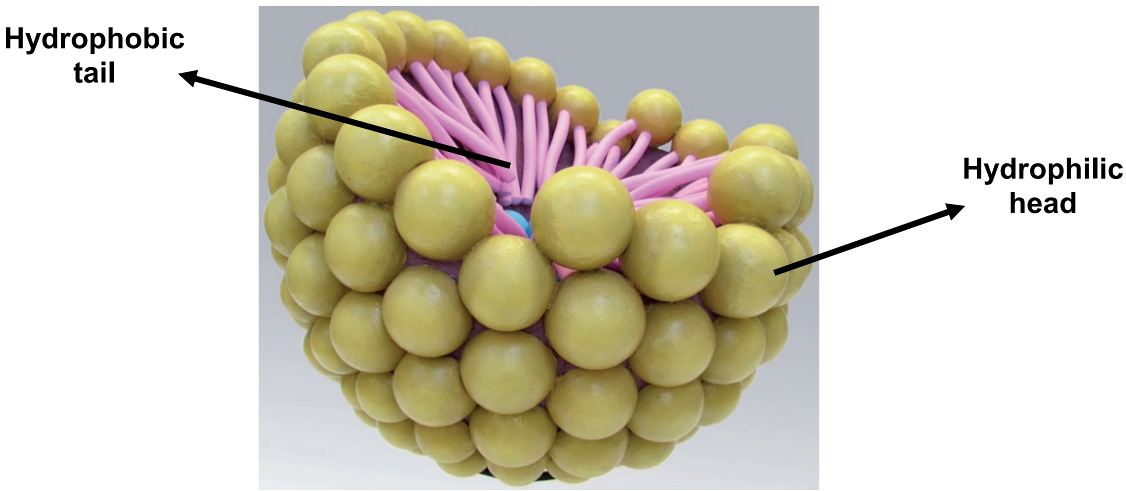


Figure 41 : A model of a micelle [169]

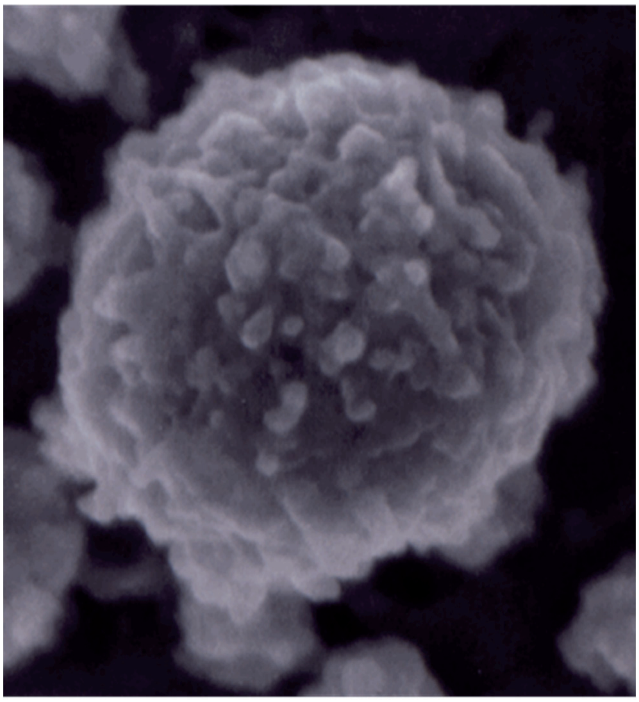


Figure 42 : A real micelle [170]

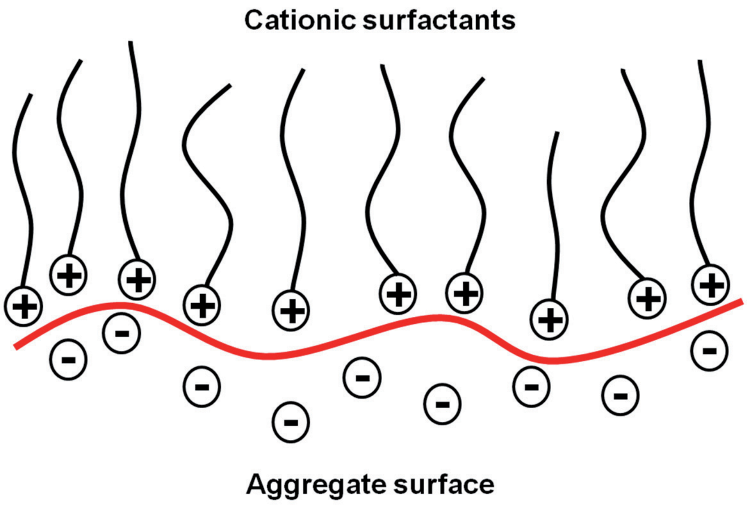
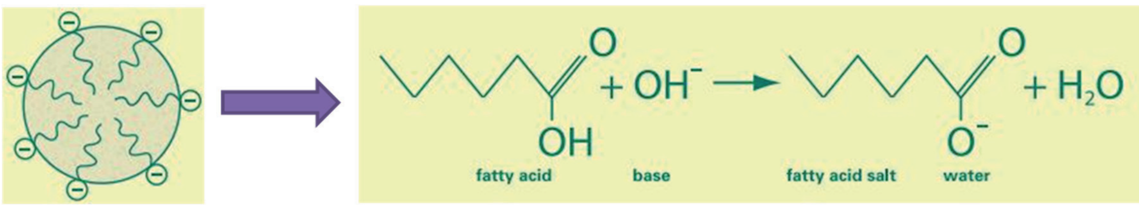


Figure 43 : Cationic surfactant and its orientation on an aggregate surface

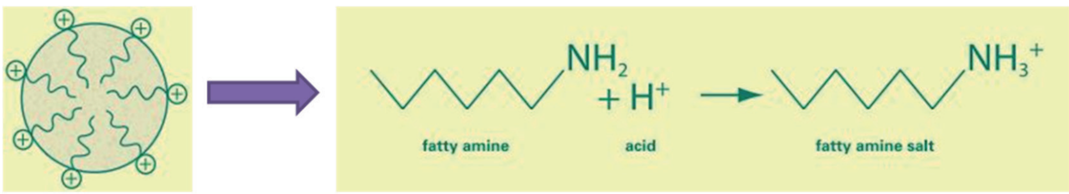
3.2.7.1.1 Bitumen emulsions

A new technology that enhances the minimization of water stripping effect, is the use of bitumen emulsions and for this purpose, a special type of emulsifier (a surfactant type) is used. Bitumen emulsion is the dispersion of minute droplets of bitumen in water (oil in water emulsion). The bitumen particles are stabilized in the suspension and may not readily coalesce due to the repulsion force as an effect of the presence of emulsifier. According to the application type, bitumen content is varied from 30 to 70 percent. In case the aggregate is basalt, dolomite and limestone (which have positive surface charges), an anionic emulsion is used which means the bitumen droplets will be negatively charged (in fact the anionic surfactant which has a negative charge polar head group, inducts this negative charge on the surface of the bitumen droplet). When the aggregate is siliceous (such as quartz, granite, sandstone and gravel) then the cationic emulsions are preferred. In cationic bitumen emulsion, the positive charge is imparted to the surface of the bitumen droplet, causing the bitumen to have a positive charge [109] [156] .

As presented in figure 44, an anionic emulsion is normally prepared from the reaction of a fatty acid with a strong base such as sodium or potassium hydroxide and a cationic emulsion is developed from the reaction of a fatty amine (nitrogen derivatives of fatty acids) with a strong acid such as hydrochloric acid.



(a)



(b)

Figure 44 : Bitumen emulsions: (a) anionic emulsion - the resultant fatty acid salt imparts a negative charge on the bitumen droplet surface and, (b) cationic emulsions - the resultant fatty amine salt imparts a positive charge on the surface of bitumen droplet [156]

Regarding the surface tension of the emulsifier, it shall be mentioned that, 1% anionic emulsifier bitumen at 25 °C has a surface tension of about 37 dyne/cm. On the other hand, the surface tension for 1% cationic emulsifier bitumen is about 34 dyne/cm (the value of surface tension depends on the type of the emulsifier, but this is just as an example to get an idea) [171].

3.2.7.1.2 Anti-stripping agents for bitumen-aggregate adhesion

Anti-stripping agents are surfactants that must have the following characteristics [172]:

1- Modify interfacial tension between aggregate and bitumen.
2- Reduce aggregate-bitumen contact angle to values smaller than 90°.
3- Allow the aggregates to be wetted by bitumen.

Generally, in order to enhance the water resistance of an asphalt mixture, different methods could be applied. Treating the aggregates, treating the binder or changing the mixture design or recipe are the main approaches in this field [142].

The addition of anti-stripping agents is a method to modify not only the aggregate surface characteristics but also the binder characteristics (but in some cases, the anti-stripping agents do not reveal the same effect in industry scale that they had in laboratory scale, or even sometimes, they have negative impacts on the asphalt mixture). The anti-stripping agent must have the ability to attach itself to the specified aggregate surface that is being used [142].

Aggregates are more or less hydrophilic (water loving) therefore they are coated with water relatively easy. On the other hand bitumen is hydrophobic or oil loving, however the fact is that many aggregates are attracted to bitumen, but not adhered to it (this attraction might not last too long). If an aggregate is coated with a thin film of water, the bitumen may cover the aggregate but will not stick to its surface, unless the bitumen replaces the water layer. The same problem exists for aggregates with dusty surfaces: there will be no strong adhesion between the aggregate surface and the bitumen. The wetting power of bitumen, which is its ability to make a connection with aggregate surface and finally completely coats it, is a function of many parameters (as discussed before) one of which is viscosity. Keeping the other influencing factors constant, the lower the viscosity of bitumen the greater the wetting power of bitumen. Bitumen is a hydrocarbon product and has a rather low surface tension, much lower than the surface tension of water. That is exactly why water has a greater wetting power (with respect to bitumen) and will wet the aggregate more easily than the bitumen and may also displace the bitumen layer that has covered the dry aggregate [142].

For an acceptable bonding between the binder and aggregate surface, the nature of the aggregate surface shall be changed and the surface tension shall be decreased so that the surface gets more lipophilic (oil loving) or hydrophobic (water hating) characteristics.

As explained before the aggregates are categorized to either acidic (limestone) or alkaline groups (quartzite). In fact, all the aggregates are a mixture of alkaline and acidic minerals, but this classification helps more or less to define their behavior. The most decisive factor is the content of silica or SiO_2. Based on experiments, the alkaline aggregates that contain lower silica content, have a better adhesion with bitumen. To clarify this issue, a brief explanation on bitumen chemistry is provided. Bitumen is a hydrocarbon product, which contains naphthenic acids (which is a polar compound). The naphthenic acid has a carboxylic acid group (R-COOH) and a hydrocarbon part (R represents a non-polar hydrocarbon alkane chain) [142].

The carboxylic acid is a chemical functional group that plays an important role in adhesion process. In the presence of water, this molecule is dissociated to $R\text{-}COO^{-}$ and H^{+} causing the bitumen surface to have a negative charge. An increase in pH of the contact water increases the dissociation of the acid molecule as well [123] [161].

When such a molecule comes in contact with an alkaline aggregate, then the carboxylic acid part will be absorbed on the surface with hydrocarbon part (CH group) pointing outward. This phenomenon changes the aggregate surface properties enough, to enable the binder to adhere to it [142].

The main disadvantage of alkaline aggregates such as limestone is that they usually get polished (areas of pavement where a part of aggregate is extended above the asphalt binder) under traffic load and therefore their application on surface course shall be avoided. The acidic aggregates such as quartzite do not normally suffer from polishing action but have another disadvantage. While they are acidic, their respond to the naphthenic acid in bitumen is very low. In fact, since both sides are acidic, they counteract each other, thus gaining a good bond between siliceous aggregates and bitumen is hard. Although there might also be alkaline contents in bitumen but since they are very weak, there will not be a proper bond to silica (another reason of not having a good adhesion bond between siliceous aggregates and bitumen) [142]. Figure 45 shows the siliceous aggregate-bitumen interface as well as the formation of the bonding. Figure 46 reveals a real electronic microscope photo of a bitumen-aggregate interface.

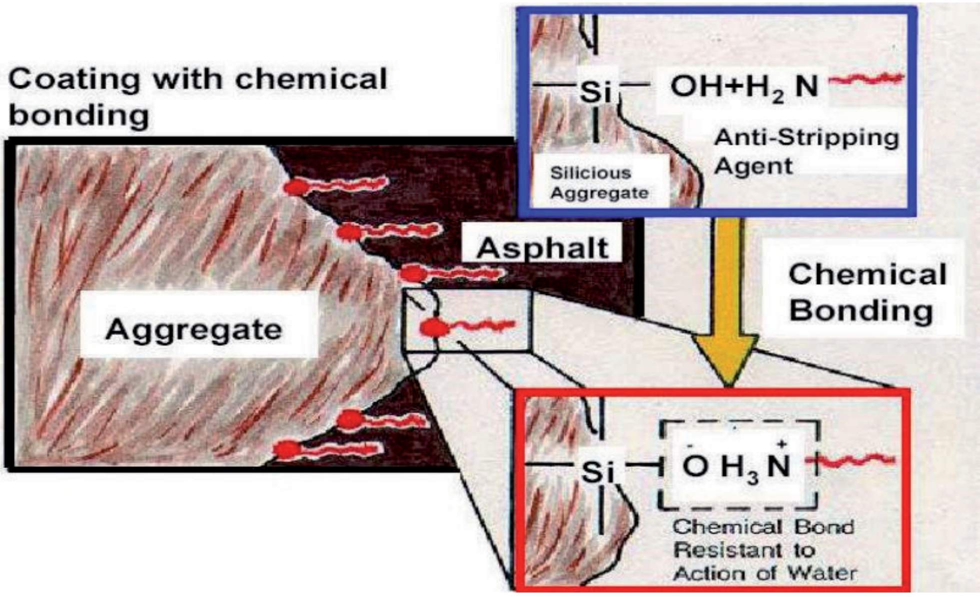


Figure 45 : Bitumen and siliceous aggregate contact [112]

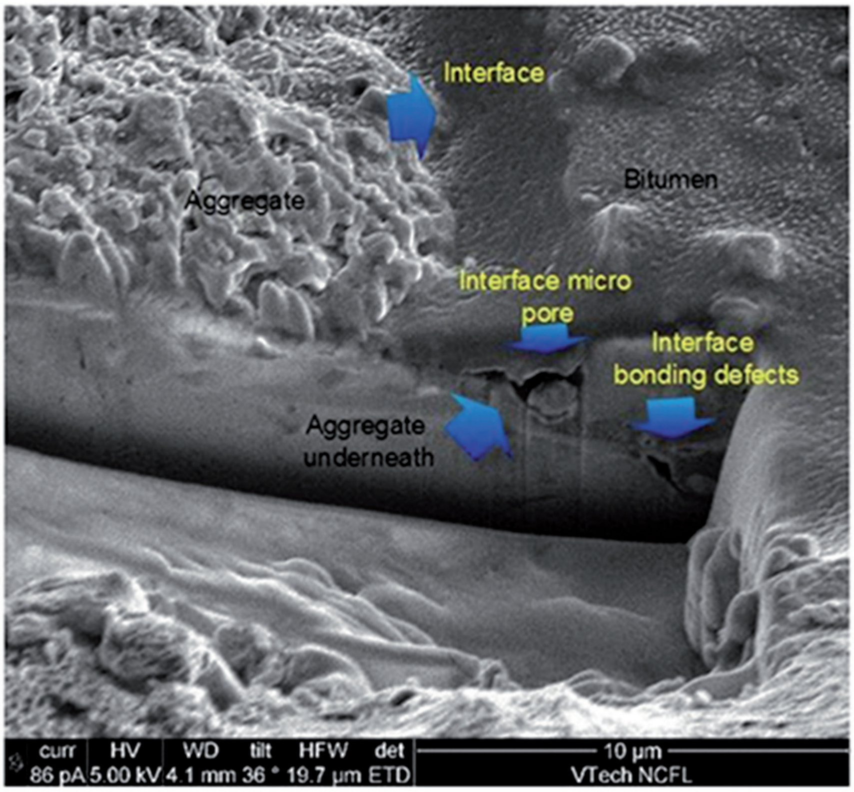


Figure 46 : Real interface view of the bitumen-aggregate system [173]

In the absence of additives, some (absorption) properties of aggregates such as surface texture and porosity might also affect the adhesion of aggregate surface to bitumen. A smooth surface aggregate do not keep the bitumen layer as good as a rough-surface aggregate. A porous aggregate that have adsorbed bitumen, will hold it better than a smooth surface one.

It is reported that the addition of heavy metal cations to aggregate surface may enhance the adhesion and improve moisture resistance (as an example, ferric naphthenate is mentioned to be significantly effective) [149].

Different types of additives such as anti-stripping agents are available in the market. They are in solid or slurry (liquid) form. Some are added to dried/wet aggregate surfaces in the dryer drum (in a form of dried powder, e.g. hydrated lime in a dosage of 1 to 2 percent of aggregate weight). Some are introduced to the materials at the mixer entrance point. A number of them are added to bitumen (e.g. liquid amines with a dosage of 0,5 to 1 percent of bitumen weight) prior to mixing phase. Apart from their addition technique, they are generally categorized into three different groups as specified below:

- ✓ Fatty amines, which are surface-active compounds, or in other words surfactants
- ✓ Iron naphthenate
- ✓ Hydrated lime or calcium hydroxide

A short description of their key information is given below [142] :

Fatty amines have long hydrocarbon chains and are the most appropriate anti-stripping agents for bitumen. As they are produced from fatty acids, therefore they are called fatty amines. The fatty amines are ionized in the presence of water to produce an amine ion (R-NH3) which has a positive charge. Thus, the fatty amines are cationic. The adhesion power of fatty amines is controlled by their length of hydrocarbon chain and their number of amine groups. Short hydrocarbon chains are less soluble in bitumen with respect to larger ones (because their bond with bitumen is weaker). An optimum performance for a fatty acid is obtained with 14-18 carbon chains amines and one or two amine groups. The number of amine groups has impact on the chemical properties of the fatty amine whereas the length of the hydrocarbon influences its physical properties. The shorter the chain the lower the melting point.

The addition of small amount of fatty amines causes bitumen to be able to wet the hydrophilic aggregates. This is due to the fact that, anti-stripping agents modify the surface properties of aggregates. Fatty amines are best used for siliceous rocks, as they form a strong and sometimes permanent chemical bond with silica, which can resist against the action of water and enhances the adhesion of bitumen-aggregate system.

Fatty amines consist of a hydrocarbon chain and an amine group. The amine group reacts with the aggregate surface and the hydrocarbon chain, which is hydrophobic, orients and directs itself toward/into the binder. As a result, the long hydrocarbon chain plays the role of a bridge between the hydrophobic bitumen surface and the hydrophilic aggregate surface thus forming and inspiring a strong bond between the two materials. Fatty acid agents may be in liquid or solid form, which has no impact on their adhesion ability. In case the agent is given manually to the binder, solid agents are used, on the other hand if the addition of agent is automatic or the binder is used at temperature below 50°C then liquid amine based are applicable.

It is very important in fatty amines applications to consider the effect of temperature on their behavior. At ambient temperature, amines may be stored for an indefinite period of time. Nevertheless, as the temperature rises, their characteristics may change, since bitumen has various amounts of acidic compounds, which can react with fatty amines. Below 100°C, the reaction is slow but above 100°C the rate of reactions is accelerated until a temperature point that the agent loses its adhesion power completely. Just to be clear, at 120°C and within 24 hours, 50% of the added amine may be inactivated, at 180°C the amine can be stored for a few hours, otherwise it loses its activity [142].

Therefore, the important parameter in regard to bitumen anti-stripping agents (which are based on fatty amines and fatty amido-amines) is that they have lack of thermal stability and are quickly degraded when mixed with bitumen and stored at high temperatures (150ºC - 180ºC) [172].

Iron naphthenate is the second class of anti-stripping agents. It is an iron salt of naphthenic acid which is a mixture of carboxylic acids. Iron naphthenate migrates to the aggregate-bitumen interface (while bitumen is still hot) and forms a water resistance complex [142].

Hydrated lime is the third class of anti-stripping agents. It may be added either in form of powder (as mineral filler) to the aggregates or in a more effective way known as slurry form (as an anti-stripping additive) prior to mixing process. The calcium hydroxide helps by consolidating the fines and clays on the aggregate surface. It also provides calcium bonding for bitumen on the aggregate surface. Based on the researches, the acid constituent of bitumen migrates toward the aggregate-bitumen surface. These acids often form salts with sodium and potassium minerals of the aggregate surface (which is prone to stripping). There exist an important fact that has to be taken into account and that is: the sodium and potassium salts, which are a kind of soap, are much more water-soluble than calcium salts of the same acid. Therefore, the application of lime slurry leads to the formation of calcium salts (hydrated lime adsorbs carboxylic acids of bitumen) at the bitumen-aggregate interface causing a more water resistant bitumen-aggregate bond and as a consequence, the material will be more resistant to water stripping and moisture damage. Hydrated lime may also change the mechanical properties of the HMA [142].

Adding about two percent of hydrated lime to the asphalt mixture may enhance the bitumen-aggregate surface adhesion significantly and as a result, the quality of the asphalted roads will be increased [174].

Based on investigations and inquiries, the use of calcium hydrate could have the following (various) advantages for asphalt mix [175]:

Increased resistance to moisture and frost damage, improved technical properties, increased aging resistance, increased wearing resistance, increased rutting resistance, increased useful life, more cost effective solution, lowering of global warming potential (less CO_2 emission) through reduction of road maintenance, reduction of recycling, less road works, less traffic jam and increase of total life cycle.

The estimated cost for a duration of 50 years shows that the total cost of asphalt with hydrated lime is less than the total cost of normal asphalt (figure 47).

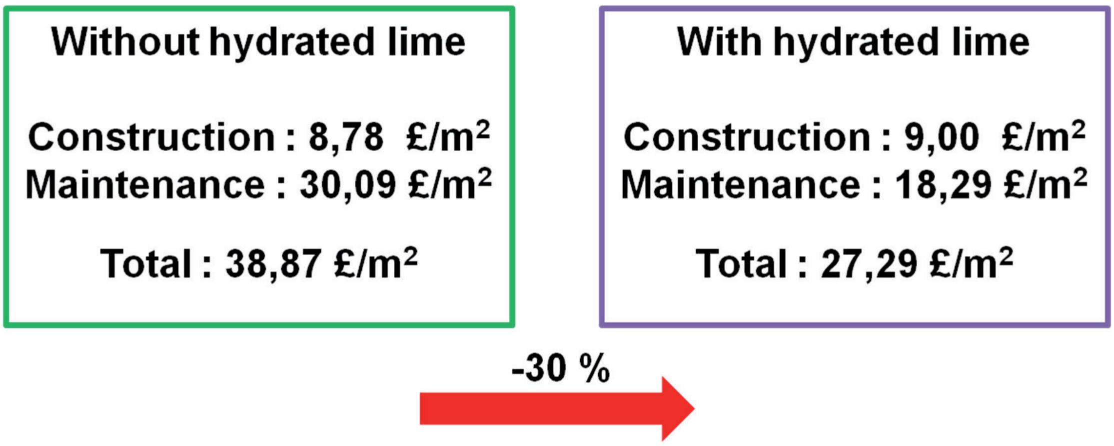


Figure 47 : Comparison between final costs of per square meter of asphalt with and without hydrated lime [175]

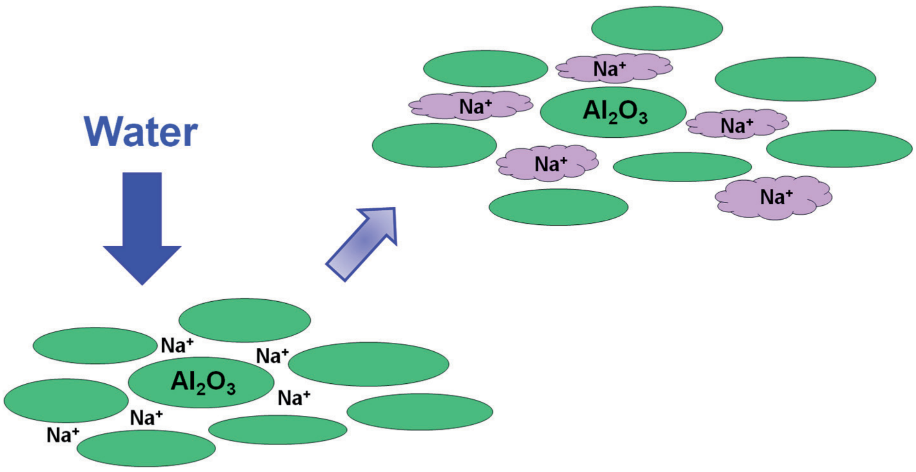
Because of the anti-stripping effect of hydrated lime, it is also regarded as an anti-stripping agent in the asphalt industry. In the USA different types of additives (such as amines, polymers, Portland cement, fly ash and flue dust) are used in order to reduce the moisture sensitivity but hydrated lime is the most widely used one. As a declaration to its huge application in the asphalt industry, one may point out to some of its additional advantages (other than its stripping reduction property) as listed below:

- ✓ acting as a mineral filler, thus helps in stiffening the bitumen and asphalt,
- ✓ changing the properties of clay fines in order to improve moisture stability and durability,
- ✓ influencing on oxidation kinetics of asphalt cement and reduce the deleterious effects of oxidation, and
- ✓ reducing resistance to fracture growth [176].

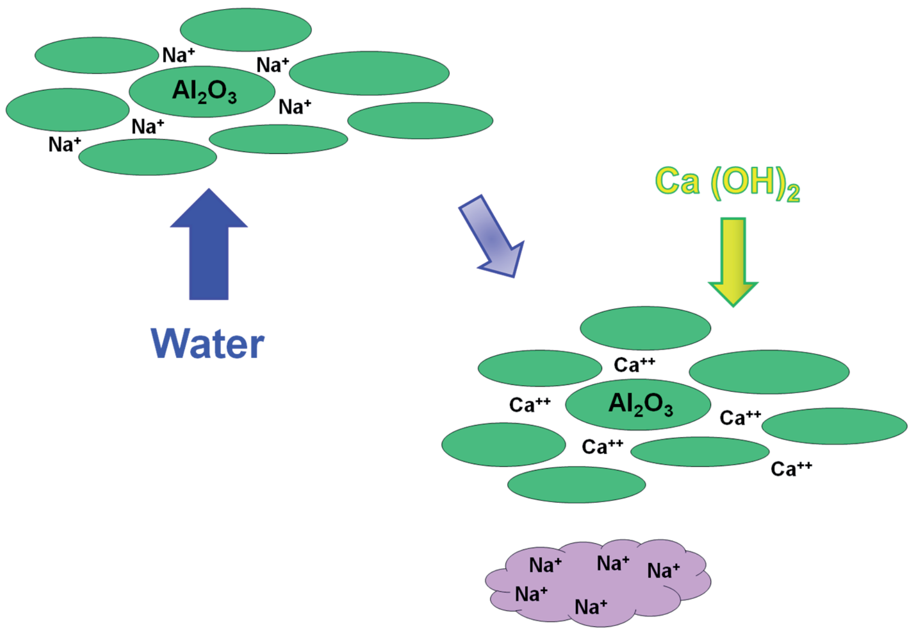
As a result of aforementioned discussion about lime (also known as quick lime or CaO) and hydrate lime (also slaked lime or $Ca(OH)_2$), it shall be noted that, lime as an additive may improve the adhesion between the aggregate surface and bitumen only when moisture is introduced to the system. Moisture activates the hydrated lime and then it influences the adhesion bonding. Hydrated lime causes a sharp decrease in interfacial tension between water and bitumen and leads to a better adhesion. It improves the resistance to stripping by interacting with carboxylic acids in bitumen and forming insoluble products that are readily adsorbed on the surface of the aggregate. Lime provides calcium ions that can replace hydrogen, sodium, potassium and other cations on the aggregate surface. Lime has been used in asphalt industry since 1910. At first, it was used as mineral filler but afterwards it was taken as an additive as well. Lime in its oxide form (CaO) and hydroxide ($Ca(OH)_2$) form is active and reacts with water quite easily, but lime stone ($CaCO_3$) is not active and does not provide the benefits which are desired as anti-stripping agent. However, limestone may be used as mineral filler. An important issue that it is worth mentioning here is that, it is better to use hydrated lime in a slurry mode rather than solid powder [148]. When the hydrated lime is added to the aggregates in a slurry form, then it has to be dried before mixing phase.

Hydrated lime also reduces the rate of oxidation and aging of the asphalt pavements [177]. The importance of the oxidation of asphalt is due to the fact that it is the main reason for asphalt hardening. On the other hand, during this hardening process many desirable asphalt performance properties are deteriorated. Embrittlement and excessive pavement cracking are two of these problems. Oxidation process produces polar function groups in bitumen. Ketones and sulfoxides are the major oxidation products. Dicarboxylic anhydrides and carboxylic acids are formed as the minor products. Therefore, minimizing the oxidation side effects could be also a notable positive point or an advantage for hydrated lime application [178].

Figure 48 and 49 show how hydrated lime affects the surface of mineral aggregates in a schematic and easy way.

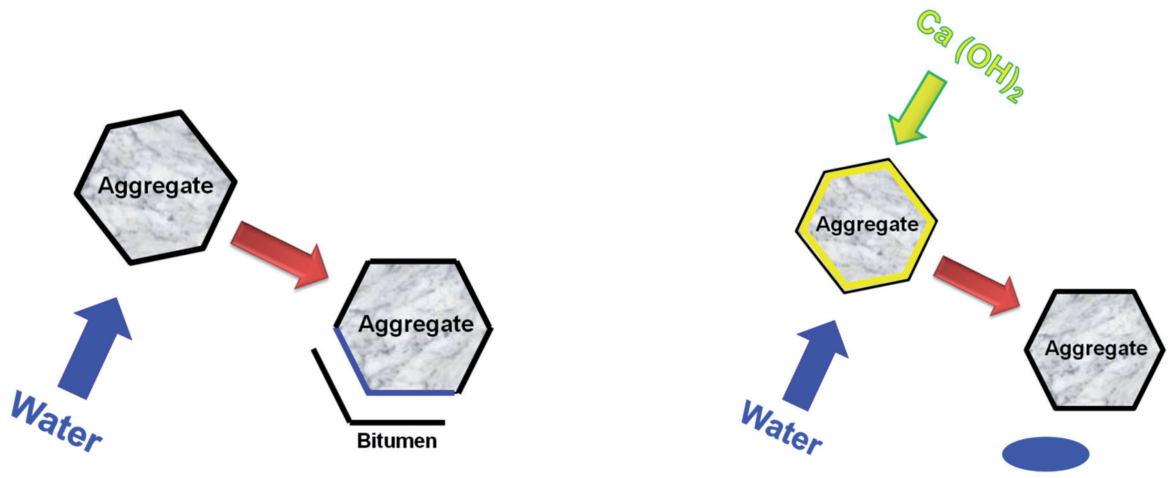


(a) before addition of calcium hydroxide



(b) after addition of calcium hydroxide

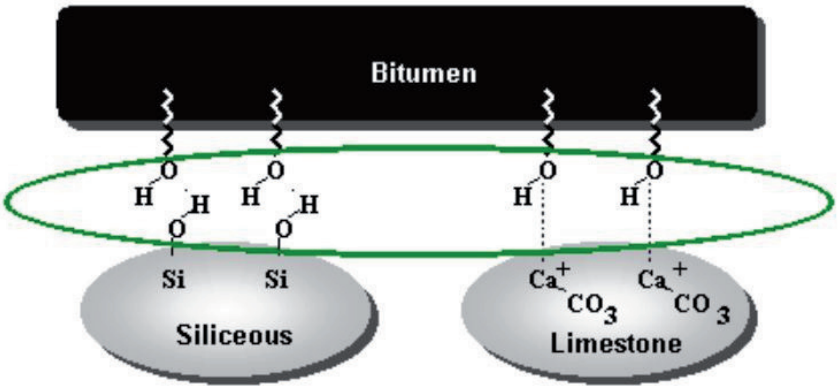
Figure 48 : Addition of calcium hydroxide (hydrate lime) to the mineral aggregates and its impact on the aggregate surface, (a) before addition and, (b) after addition [179]



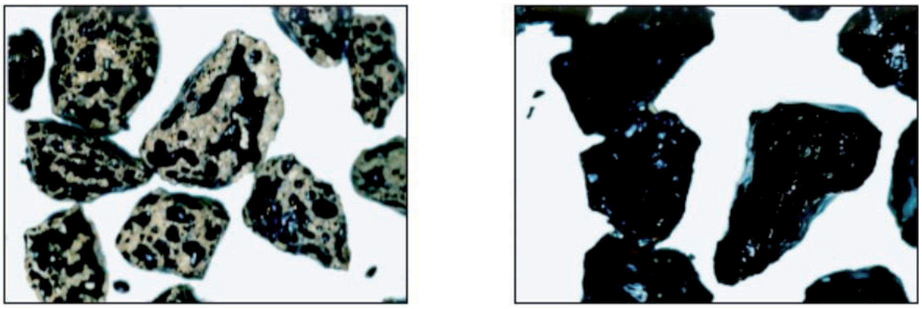
(a) before (b) after

Figure 49 : An aggregate surface (a) before and, (b) after the addition of calcium hydroxide [179]

Figure 50 depicts how the adhesion bond between an (acidic and alkaline) aggregate surface and bitumen, by means of anti-stripping agent takes place. Afterwards, the effect of these agents on real aggregate surfaces (with and without additive) is shown. As it is clear, the use of anti-stripping agents has a great influence on the adhesion bond between the aggregate surface and bitumen and it is independent from the aggregate type. In case of not using these agents, the bitumen film is stripped off from the aggregate surface. It is also important to mention that, for each aggregate type and based on its characteristics the right agent must be used otherwise it may have adverse impact on the behavior of the whole system.

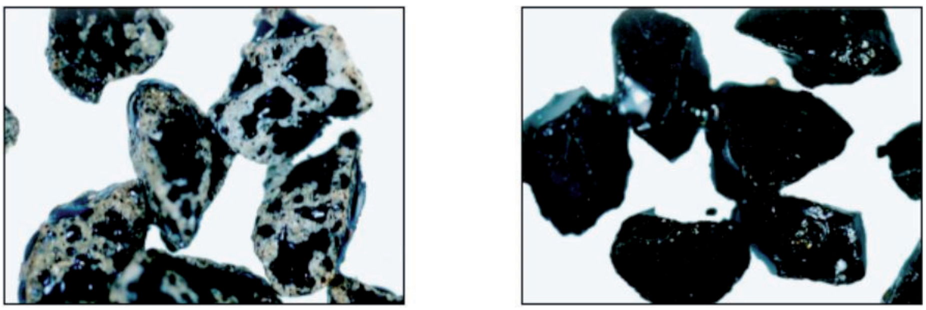


(a)



Quartz

not doped doped



Limestone

not doped doped

(b)

Figure 50 : Formation of adhesion bond between aggregate and bitumen by means of anti-stripping agents. (a) the formation of adhesion bond between acidic/alkaline aggregates and bitumen by using anti-stripping agents and, (b) the effect of anti-stripping agents on stripping of bitumen layer from two types of aggregates (acidic and alkaline) in two situations: doped and not doped with anti-stripping agents [172].

3.2.8 An overview and a brief discussion on the foregoing operations in asphalt plants and their challenging problems

Based on literature review, our pilot scale studies and experiments performed with respect to this research project, it was revealed that there is a correlation between the thermal process of aggregates-bitumen treatment and the asphalt quality. The solution approach is based on the correlation between thermal treatment of the asphalt production process and the behavior of the minerals and respectively the aggregates. In manufacturing the hot mix asphalt (HMA), the mineral mixture or aggregates, depending on the asphalt type, are mixed together due to a special recipe and with a prescribed proportion of different grain size fractions, and then heated up for a few minutes in a continuous process. Generally (as will be discussed fully in chapter 9 of this thesis), the heating takes place in a dryer drum mixer with burner system. The aggregates are heated up to 230 °C and in case of recycled asphalt the aggregates temperature reach up to 320 °C. Afterwards they are screened in a hot state for more precise dosing. The sieved hot aggregates are then mixed with bitumen, which has a temperature of 160 to 180 °C. As a result of this mixture, the asphalt concrete (AC) is produced. The type and amount of added bitumen depends on the desired type of asphalt. The product is then transported to the construction site and is used for paving. Depending on the distance between the construction site and the asphalt plant, transport may take up to one-hour time.

Mineral resources apart from their origin, contain different forms of water. Humidity, capillary water, pore-water, gel water, bound water, and crystal water are various types of water that may be present in a rock.

As mentioned before, aggregates are heated up to 230 °C or even in case of recycled asphalt 320 °C for asphalt production. According to their grain size, they will reach different temperatures. Smaller grain sizes are fully heated while the core of the coarse grains possibly has not reached the sufficient temperature or in other words, the bigger grains have not gained enough heat. Our own studies show that aggregates (at the same temperature as above) will emit their internal water in the form of water vapor for several hours. The evaporation time depends on the size, type, time being heated, temperature being heated, final core temperature and the porosity of the grains.

What happens in the bitumen-aggregate mixer is that exactly in the situation and time interval that the water content of the aggregates is still evaporating out from the grains (specially the coarse grains), the bitumen is added to the aggregates. As a result, a countless number of bubbles are created which displace the bitumen and partially avoids the wetting of the evaporation-spots (evaporation vents) on the aggregate surface. Therefore, the aggregate surface is not fully covered by a constant thickness of bitumen film.

Figure 51 (based on our own experiments) shows the result of an electronic microscopy of an aggregate surface after the addition of brown bitumen. The generation of bubbles and craters as a consequence of vapor discharge is distinguishable.

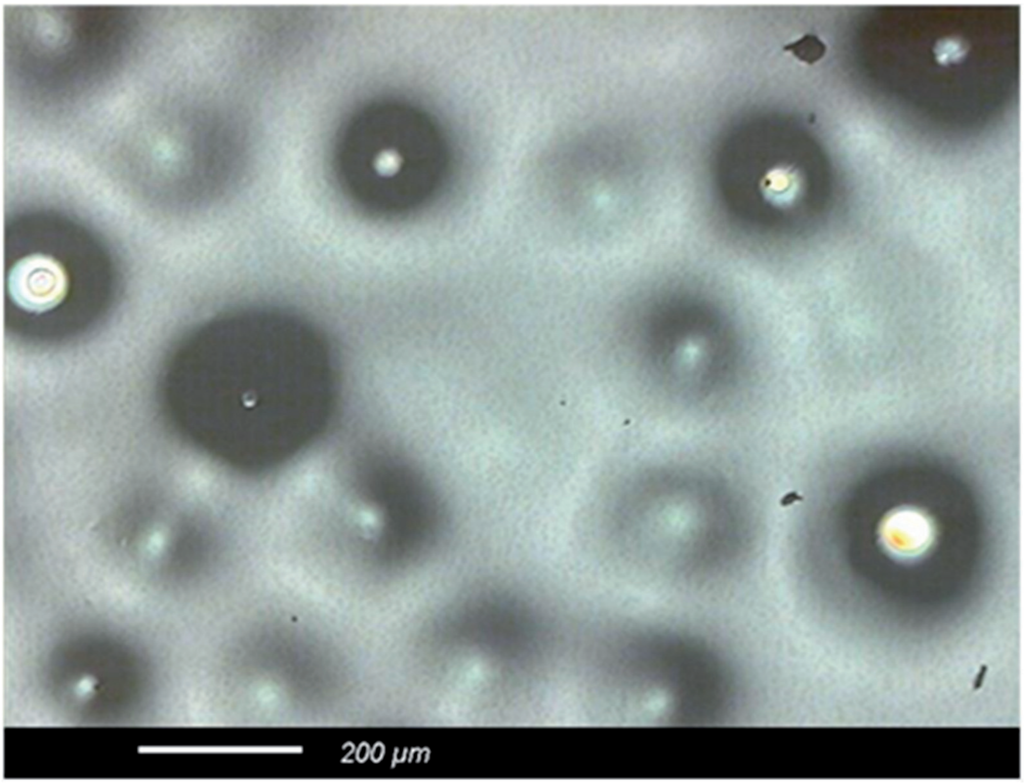


Figure 51 : Bubbles and craters created on the surface of bitumen layer on the aggregate surface as a result of water evaporation (after aggregate is mixed with bitumen and dried in room tempereture)

Prior to asphalt paving and even until asphalt is partly cooled down after the paving, vapor pressure decreases, thus small bubbles are produced at the interface area between the (aggregate) grain surface and the bitumen, which cannot burst. Consequently, the bitumen is further displaced and the wettability (by bitumen) is reduced. From a certain point of temperature reduction, the exiting water vapor is condensed on the interface/boundary and forms a condensed surface layer. This is a circumstance that later increases the hydraulic conductivity and permeability on the boundary surface. The current practice of asphalt production, inevitably leads to the formation of open pores at the interface in such a way that the water will easily reach the grain surface or boundary layer later on. The described effect of cavity/opening formation mechanism through the not burst bubbles as well as through the condensed water vapor originated layer at the boundary layer, will help to increase the hydraulic conductivity. In Figure 52 the stripping (separation) of the bitumen layer after a conditioning period (by means of submerging/immersing in water) is visible.

Figure 52 : Stripping phenomenon of bitumen coating after conditioning of samples (submerged in water)

The described fact of adhesion deterioration (stripping of bitumen) due to vapor discharge from the most abrasive grains, leads to a second problem which makes it noticeable in the asphalt quality issue (discussed below).
Bubble formation leads to the generation of craters, therefore the effective surface area between the bitumen layer of a grain and the next grain is reduced. Thus, the cohesive strength between the bitumen-bitumen surfaces of two grains next to each other is

decreased (this phenomenon is known as raveling of asphalt which is due to loss of asphalt binder).

In addition to this, after the asphalt paving and because of the weather condition, the water enters through originated bubble holes in bitumen film and (infiltrate) goes between the bitumen-aggregate surfaces (interface area). Thus, the adhesion strength at the interface between bitumen and aggregate (known as affinity) will be disturbed (stripping phenomenon). Based on our own experiments, the poorer the quality of the aggregate the faster it is to notice. In case of water sensitive types of rocks, this problem can act so quickly that shortly after the asphalt paving, the asphalted road surface layer must be removed again.

In the aggregates which undergo an overheating process and experience severe out drying, the latter described problem is intensified (based on our own studies). Special aggregates, whose rock strength is greatly reduced due to water adsorption, shall not experience any overheating (our own studies). This is the case, which inevitably occurs for the fine particles (fines) and very small grains in many of the current asphalt production processes. After our own initial investigations, from the aggregate point of view, the quality of asphalt depends on the following factors:

- ✓ Mineralogy
- ✓ Physical characteristics such as porosity and surface roughness
- ✓ Surface chemistry
- ✓ Grain size
- ✓ Water content
- ✓ Heating temperature (in dryer drum)
- ✓ Storage duration of the hot aggregates in silos (prior to their mixing with bitumen and respectively asphalt production)
- ✓ Asphalt final product retention time until construction phase (transport duration from the asphalt production plant to the asphalt construction site and consequently starting the paving process)

3.2.9 Aim of the research

As explained in the previous sections, the asphalt industry has been encountering the asphalt quality problems since decades. Stripping, rutting, raveling, cracking, etc. of asphalt pavements have been an important problem since long ago. Different researches, articles, PhD thesis and master thesis have been written on this subject but the problem is still unsolved.

The characteristics, chemical and physical properties of different kinds of aggregates and bitumen must also be under concentration. Many publications exist with regards to the aforementioned themes but most of them discuss these items separately and not in connection with one another, e.g., many papers are published on the quality of rocks but the relationship between the rock quality and asphalt quality is missing. Many researchers have also studied the use of various additives to enhance the adhesion between the bitumen binder and aggregates. However, what is really missing is any kind of effort that tries to solve this problem only and only on the basis of aggregate characteristics itself. Changing the type of aggregates and bitumen or using different types of additives is not the aim in this research.

Considering this issue, the main aim of this part of the research is to find out the relationship between the thermal processing of aggregates and the asphalt quality. The asphalt quality itself is a function of aggregate quality, aggregate water content, temperature, and the duration of thermal treatment. Based on the preliminary lab-scale experiments, detailed investigations on the quality of aggregates (fist part of this thesis) play a significant role on this challenging matter. I also obtained very good results through the use of microwaves as our new developed alternative option for asphalt production, but to make this work short and concise, it was decided not to include them in my thesis.

The natural stone industry as well as the asphalt production plants shall be shifted up in a position to be able to produce higher asphalt quality through:

I. Careful selection of the natural crushed stone (aggregates)
II. Suitable thermal treatment of bitumen-aggregate system

As a result of implementing the aforementioned factors, not only the quality of the asphalt pavements will increase but also the asphalt production companies will experience a reduced number of complaints which leads to an increase in their profitability and competitiveness.

4 Basalt-Actien-Gesellschaft

4.1 Introduction

Basalt-Actien-Gesellschaft (BAG) is a basalt stocks corporation with vertical integration structure. With more than a century of tradition and over 150 affiliates, counts BAG the leading building material manufacturer in Germany. The main field of BAG activity is the production of aggregate and asphalt for the construction industries such as roads, highways, airport runways, hydraulic constructions, and railways. Other business fields of BAG are as follows: recycling, land-filling, re-cultivation, concrete transport and logistics [180].

BAG is active in international scale and in order to fulfill its objectives, it owns many quarries in Germany and abroad. Novel mining methods together with modern production plant, special know-how of the technical staff, quality perfection of the products, good delivery service and customer satisfaction are the building blocks of their successful business.

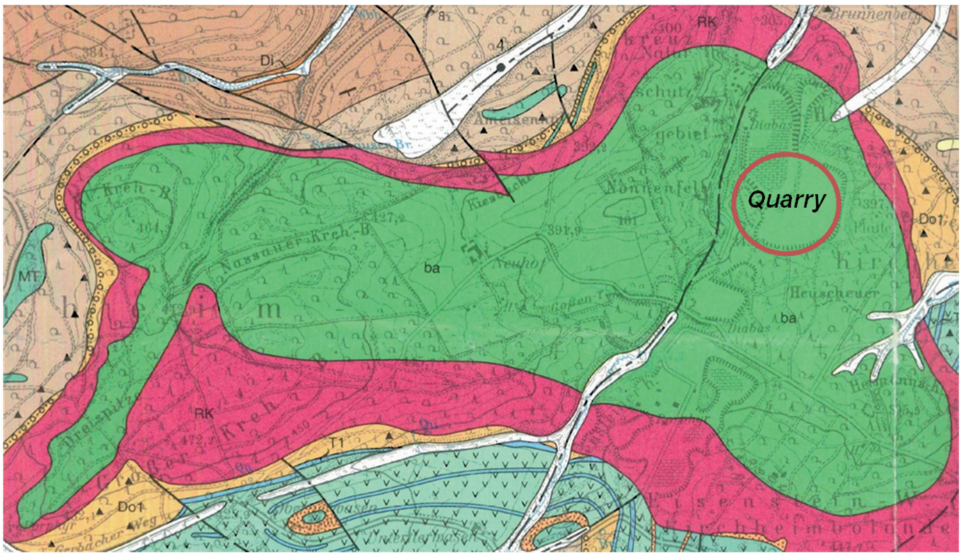
4.2 Quarries

Two of BAG quarries will be our case studies in the course of this study. They have been active since decades and both of them produce building materials (mainly aggregates for concrete, asphalt and railway ballast). The spectrum of their aggregate varies between 0 to 56 mm.

Our main focus will be on the first quarry. However, the second quarry will be used to validate our obtained results from the first quarry. Figure 53 gives an aerial view of the first quarry [181].

Figure 53 : An aerial view of the first quarry [181]

The first quarry is located within a basic intrusive body mass mainly from basaltic andesite and tholeiitic basalts, which has generally a fine-grained matrix [182] (figure 54).



Basic intrusives	ba	Basaltic andesite and tholeiitic basalts, gray-black, fine-grained matrix of plagioclase, little pyroxene, inclusion of altered olivine
Kuhkopf-Dom	RK	Dacite to alkali-feldspar trachyte, medium gray, light red to whitish weathered, dense matrix with inclusions of sanidine and biotite

Figure 54 : Geological map of the first quarry [182]

4.3 Recent problems in production

As mentioned before, both quarries produce natural crushed stone (aggregate) for different construction purposes, such as concrete, asphalt, railway ballasts, and so on. In the recent years, the production line has encountered a tremendous problem, namely the rock quality.

For all mentioned purposes, the quality of the rocks or aggregates must meet the set standard. These standards are defined separately by each country (via standards such as DIN-Norm). Nevertheless, each state may also have its own additional related requirements and regulations. In our case, the general standards are not only specified by German DIN-Norm but also by the state.

The major encountered problems lie in the quality of rail ballasts and asphalt. The rail ballasts tend to disintegrate and break-down in short/long term periods and on the other hand the asphalted roads produced from the corresponding aggregates have a swelling and loss of stability values greater than what is allowed by the defined standards (with respect to the standards of the related state). Therefore, from the rock-quality point of view, the main challenge in both of these quarries is focused on two types of products: railway ballasts and asphalt aggregates. The quality failure in the mentioned products has originated serious problems for the quarries. It has caused not only customer/market loss but also high penalties in form of compensations for the company.

Based on the aforementioned difficulties, an extensive long-term research and supervision program was planned to distinguish and overcome the problem, which will be fully discussed in next chapters.

4.4 Work breakdown structure (WBS)

To have a better view of the scope of this research project and to define the fundamental steps of our final goal, the “work breakdown structure” method has been used. In fact, WBS links what we are making to how we will make it.

WBS is a type of flow-chart in a hierarchical format, which presents different steps of a project. It shows which steps shall be exactly taken to end up with the desired goal. Therefore, the project shall be broken down to its unique parts. When each of these working packages is completely done and tested, then they are put together and thus the project will be fully accomplished. Final checking of the results shall not be forgotten. The proper action plan must be taken as the next step [5].

For this research project, two different WBSs were adopted: one for aggregates quality and the other one for asphalt quality. As mentioned before, in the field of aggregates quality, finding an index (or indices), which is applicable on-site, would be of great interest. Therefore, in this research work a huge focus is given to this operational constraint (being applicable on-site).

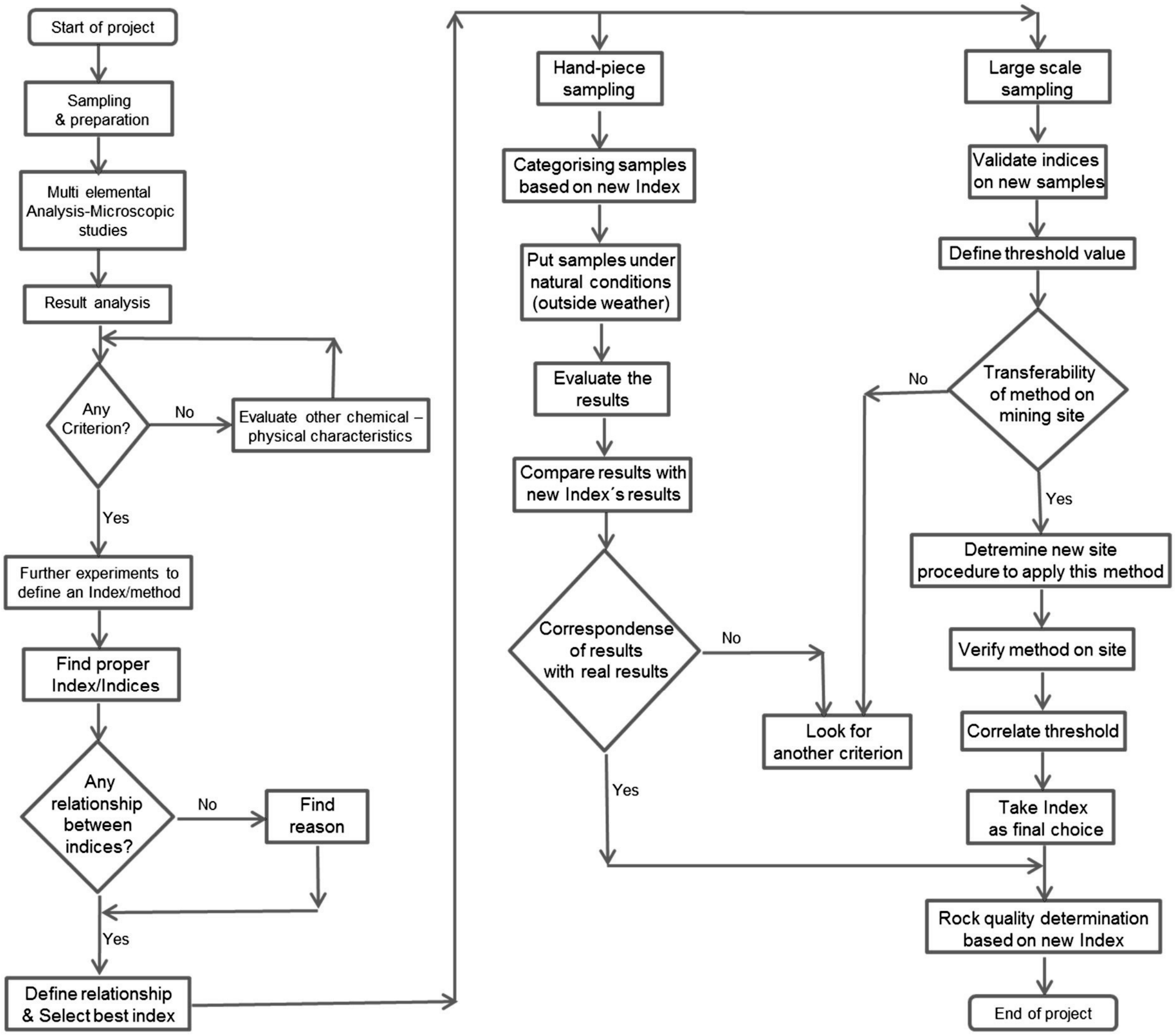


Figure 55 : WBS for aggregate quality index/indices

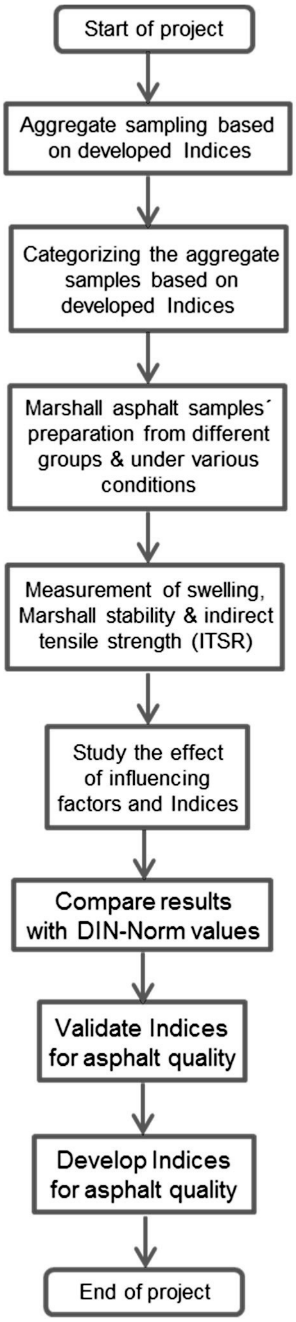


Figure 56 : WBS for asphalt quality index/indices

4.5 The need of a global quality management system at BAG

BAG is a company acting on a global scale, desiring clearly to grow. Therefore, the company is in an increasing area of tension between global standardization and flexibility in the interaction with different regions. In this path, we face more different quality awareness, connected to problems and standard differences, which needs to be taken care of. The implementation of a worldwide BAG quality control/assurance system

(QA/QC system) and consequently a permanent quality improvement system based on this research is therefore strongly advised.

Quality control processes and quality control methods (based on the following inquiries) shall be presented in a central standardized BAG quality assurance system. They are binding regulations for every quarry, mineral processing plant, and asphalt production plant.

The quality culture, quality thinking, and quality management concept shall be used during daily work in the future and the staff members have to be aware of their responsibilities for quality aspects. Besides the work on a common standard, a common quality strategy, and a common quality objective, BAG quality culture will represent their values, in an open-minded handling of mistakes and an integrated communication.

A group-wide organizational structure shall be implemented to ensure an efficient and effective coordination of the responsibilities between quality control and quality inspection units.

5 Reconnaissance study

As mentioned in the last chapter, both quarries suffer from lack of aggregate quality. We decided to use the first quarry as the reference for the first step of our studies. Work would be started there and then the results (regarding ballast and asphalt quality) would be checked for transferability to the second quarry (which is located in a completely different geological district). Therefore, in this phase, we planned to perform basic research on the lithology of the quarry to learn more about its specifications. To organize a reconnaissance study program the following steps were taken:

1- Primary field sampling

2- Sample preparation

3- Multi-elemental analysis

4- Microscopic studies

The results of these studies were useful to gain a better understanding of the problem. In fact, the main aim of this stage was to find out whether or not there is a clue that could be used to recognize this problem, potentially even prior to blasting and production.

5.1 Field sampling

Based on the negotiations with the company, five different grab samples were taken for reconnaissance studies (figure 57).

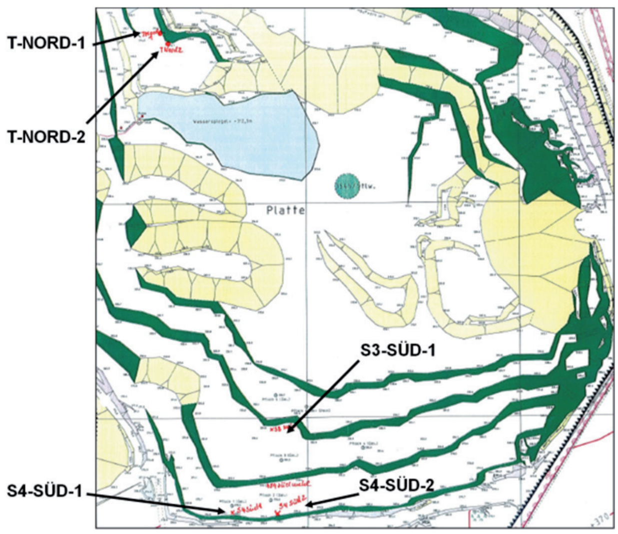


Figure 57 : Sampling locations in the quarry

As shown in figure 57, grab samples were hand-piece samples and primarily from the 1st, 3rd and 4th bench.

Table 6: Sample data

Sample ID.	Abbreviated ID.	Bench	Visual quality evaluation
T-Nord-1	T-1	1	Good
T-Nord-2	T-2	1	Good
S3-SÜD-1	S3-1	3	Poor
S4-SÜD-1	S4-1	4	Poor
S4-SÜD-2	S4-2	4	Good

In table 6, overall information about the location of the samples is presented; a visual quality evaluation is also mentioned for each sample. This evaluation is done by quarry´s staff based on their experience.

5.2 Sample preparation

The five grab samples were then taken to mineral processing lab for further preparations. They went through primary and secondary crushers and were finally milled to a size of 63 µm by a rod mill. Each sample was then divided in order to obtain a representative homogenous sample of it. While crushing the samples, there was a feeling that some were rather hard while others were more easily crushed. This perceived difference, gave us the idea of calculating a “Bond Work Index” (the energy used grinding per unit mass, KWh/ton) for each sample, however, due to the amount of time the Bond Work Index estimation takes, in the end it was disregarded.

5.3 Multi-elemental analysis

After the division process, about 30-40 grams from each individual sample were sent to chemical lab in Canada for multi-elemental analysis. There, the samples were analyzed for their constitutive compounds/elements with the ICP (Inductively Coupled Plasma Mass Spectrometry) method. The results of the main oxides in each sample and their corresponding LOI´s (loss on ignition at 850°C) were of our primary interest, therefore only a summary of the analysis is shown here in table 7. The first piece of information gained from the multi-elemental analysis was that the samples had more than 52% SiO_2, meaning, they were exactly on the line between mafic and intermediate igneous rock.

Table 7: Multi-elemental analysis results

Analyte Symbol	SiO_2	Al_2O_3	Fe_2O_3(T)	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
Unit Symbol	%	%	%	%	%	%	%	%	%	%	%
Detection Limit	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,005	0,01	
Analysis Method	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	GRAV
T-1	54,74	16,91	7,80	0,13	4,46	6,10	3,60	2,40	0,941	0,21	0,588
T-2	54,36	17,02	7,90	0,12	4,52	6,77	3,42	2,31	0,908	0,20	0,896
S3-1	52,34	16,99	8,09	0,13	4,63	7,84	3,09	1,71	1,126	0,28	2,170
S4-1	52,44	17,73	6,78	0,12	4,83	7,68	3,22	1,84	1,182	0,25	3,500
S4-2	54,63	16,94	8,28	0,13	4,20	6,66	3,46	2,52	1,199	0,33	0,523

5.3.1 Interpretation of the results

By reviewing the multi-elemental analysis, it is clear that the main differences in the rock makeup are revealed in calcium, sodium, and potassium oxide levels. At the same time, the LOI percentage is also playing a significant role. The CaO amount in samples S3-1 and S4-1 was greater compared to the other three samples, while at the same time, their Na_2O and K_2O amounts decreased analogously. Going one-step further, the LOI percentage also obeys this rule; where CaO increased, the LOI is augmented as well, and vice-versa (table 8). As mentioned previously, the LOI value represents the amount of volatile materials e.g., carbon dioxide, moisture, crystal water, bound water, carbonates, sulfates and to some extent, clay minerals. Based on the experience of the quarry´s staff, samples S3-1 and S4-1 were selected as "bad" quality samples. The primary studies done on the relationship between amounts of calcium, sodium, and potassium and the LOI value confirmed these visual quality assessments. The multi-elemental analysis showed that these two samples are richer in calcium and poorer in sodium and potassium. Their volatile amount (volatility) is also higher than the other three (up to several times). As a result, we deduced that the “hydrothermal alteration” process has taken place here. The hot, aqueous solution has lead to ion exchange between Ca, Na and K. The degree of this alteration is measured through the ion exchange process. The more Na and K ions that are replaced by Ca, the stronger our alteration process.

At first glance, we concluded that the disintegration and breaking down of the rocks could be a consequence of alteration, which reveals itself through the ion exchange process and the LOI amount. The Ca, Na and K percentages are obtained using a multi-elemental analysis and the LOI are calculated by using a muffle oven. Therefore, the amounts of Ca, Na, and K, as well as LOI, are observed to be two indicators used in identifying rock quality. To further prove the validity of this observation, we carried out additional investigations.

Table 8: Correlation between oxide contents and their corresponding LOI values

Analyte Symbol	SiO_2	Al_2O_3	Fe_2O_3(T)	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
Unit Symbol	%	%	%	%	%	%	%	%	%	%	%
Detection Limit	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,01	0,005	0,01	
Analysis Method	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	GRAV
T-1	54,74	16,91	7,80	0,13	4,46	6,10	3,60	2,40	0,941	0,21	0,588
T-2	54,36	17,02	7,90	0,12	4,52	6,77	3,42	2,31	0,908	0,20	0,896
S3-1	52,34	16,99	8,09	0,13	4,63	7,84	3,09	1,71	1,126	0,28	2,170
S4-1	52,44	17,73	6,78	0,12	4,83	7,68	3,22	1,84	1,182	0,25	3,500
S4-2	54,63	16,94	8,28	0,13	4,20	6,66	3,46	2,52	1,199	0,33	0,523

5.4 Microscopic studies and their interpretation

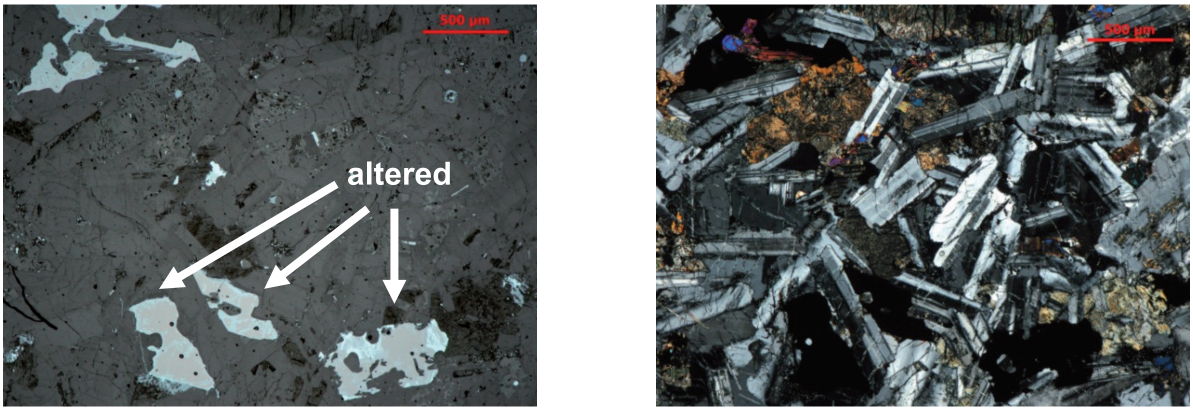
At this stage, for each of the five samples, again 30-40 grams of a homogenous powder, as well as a smaller size rock (gravel size) was given for microscopic studies through thin/polished sections. The aim of this investigation was to find out about the constitutive minerals, as well as their formation, structure, phases and characteristics. A summary of the microscopic studies is presented in table 9.

Table 9: Short summary of microscopic studies

Sample ID	Bench	LOI	Microscopy description
T-1	1	0,588	Fine grained micro-gabbro
T-2	1	0,896	Fine grained micro-gabbro
S3-1	3	2,170	Coarse grained micro-gabbro
S4-1	4	3,500	Coarse grained micro-gabbro
S4-2	4	0,523	Coarse grained micro-gabbro

The primary information gained by the microscopic studies (performed in reflected and transmitted light) showed us that (from grain size point of view) there are two categories; fine-grained and coarse-grained. Samples, mainly gathered from the 1st bench are fine-grained micro-gabbro, whereas samples from other benches are coarse-grained micro-gabbro. In another words, samples from the 1st bench have smaller crystals than the others. The rocks are categorized in an andesite-basalt group. The second piece of information acquired in this stage, is about the weathering and alteration of the samples. The microscopic studies with reflected light reveal that the alteration process had taken place and it is associated with the alteration of magnetite to hematite. In other words, magnetite is oxidized and becomes hematite. The amount of this alteration is proportional to the amount of the oxidized magnetite, which means the more advanced the alteration is, the greater the amount of magnetite that is converted to hematite. Therefore, samples with higher values of LOI have a greater transformation of magnetite to hematite.

Figure 58, shows a polished thin section of two of these samples in reflected light (left) and transmitted polarized light (right). Sample S4-1 is altered, which means the magnetite mineral was hydrothermally altered and transformed into hematite. However, sample S4-2 shows that the magnetite mineral is preserved and much less altered. Magnetite, in reflected light, is brownish-grey, while hematite is a light bluish-grey. Both are opaque minerals and appear dark in transmitted light.



(a)

(b)

Figure 58 : Photomicrographs of polished thin sections of samples (a) S4-1 and, (b) S4-2 in reflected light (left) and transmitted light (right). Sample S4-1 is an altered sample (magnetite is transformed to hematite) whereas sample S4-2 is pretty fresh and the magnetite mineral is not altered. S4-1 has an LOI value of 3,5% and MAG value of 1,220x10^{-3} SI Units, the LOI of S4-2 is 0,523% and its MAG value is 9,508x10^{-3} SI Units

Based on the preliminary information gathered up until this point of the study, the alteration of magnetite to hematite in the (namely) poor quality rocks, acts as a good clue of detecting the problem. To assess the magnetite content of a sample, the "magnetic susceptibility" of the sample is measured. We evaluated this unit using a hand-held magnetic susceptibility meter (figure 59).

Figure 59 : Hand-held magnetic susceptibility meter [183] [184]

The magnetic susceptibility of a sample is measured with this hand-held device both quickly and easily. The compatibility of this method of performing measurements on rock samples, as well as powder samples, must be studied and confirmed in order to be able to correlate the results between different forms of a unique sample (rock form versus crushed/milled form). In this stage, the reconnaissance studies will continue by applying the magnetic susceptibility parameter to our assessments.

5.5 Magnetic susceptibility measurements

In this phase, we measured the magnetic susceptibility of the five grab samples. In order to do so, the samples were first crushed and milled and then filtered through a 1mm sieve. The samples under 1mm in size were taken for magnetic susceptibility measurements. The susceptibility of each sample was read at least ten times and then averaged. To see an overview of the results, please refer to table 10.

Based on the magnetic susceptibility evaluations and the prior results, we assumed that samples with higher values of magnetic susceptibility have the potential of having a higher quality, while samples with lower magnetic susceptibility have a poor quality. As explained before, this is due to the oxidation of magnetite to hematite as a result of hydrothermal alteration [185] [186]. The magnitude of the magnetic susceptibility value is associated with the extent of alteration of magnetite to hematite.

Table 10 : Magnetic susceptibility of the samples and their LOI values

NO.	Sample ID.	MAG $_{(d<1mm)}$ ($x10^{-3}$ SI Units)	LOI (%)	Microscopic analysis	Visual quality assessment
1	T-1	5,799	0,588	Fresh	Good
2	T-2	4,492	0,896	Fresh	Good
5	S3-1	3,350	2,170	Altered	Poor
4	S4-1	1,220	3,500	Altered	Poor
3	S4-2	9,508	0,523	Fresh	Good

5.6 Results and discussions

The results of this study gave us three clear criteria that can be used to assess quarry rock quality:

- ✓ oxide content of sodium, potassium and calcium
- ✓ value of loss on ignition (LOI)
- ✓ magnetic susceptibility

In fact, these three parameters can be applied to help to solve this problem [29] [185] [186] [187]. However, since the measurement of sodium, potassium and calcium content of the samples need too much time, the main consideration will be on the loss on ignition (LOI) and magnetic susceptibility (referred to as MAG from now on) of the samples, which are easier to apply. Of course, the most useful method is to use the magnetic susceptibility because it only needs a portable hand-held device, it can be used in the field, and it delivers results in almost real-time.

The evaluation of these two parameters (LOI and MAG), with respect to the results of electronic microscope and visual assessments, showed that the fresh samples, which have no tendency to degradation and decomposition, contain a low LOI value and a high MAG content (due to the existence of fresh magnetite). On the other hand, the altered samples, which will decay and degrade, have a high LOI and low MAG due to the alteration of magnetite to hematite. Furthermore, they show a reverse relationship with one another; the increase of one results in the decrease of the other. As obvious from table 10, the magnetic susceptibility of the samples varies from 1,220 to 9,508 ($x10^{-3}$ SI Units) and their corresponding LOIs have a variation of 0,523 to 3,50 percent. The LOI of fresh rocks is considerably lower than the LOI of the altered ones and vice-versa; the MAG of the fresh rocks is significantly higher than the altered rocks. Figure 60 shows this effect in the five different samples. As it is presented, when one parameter increases, the other decreases.

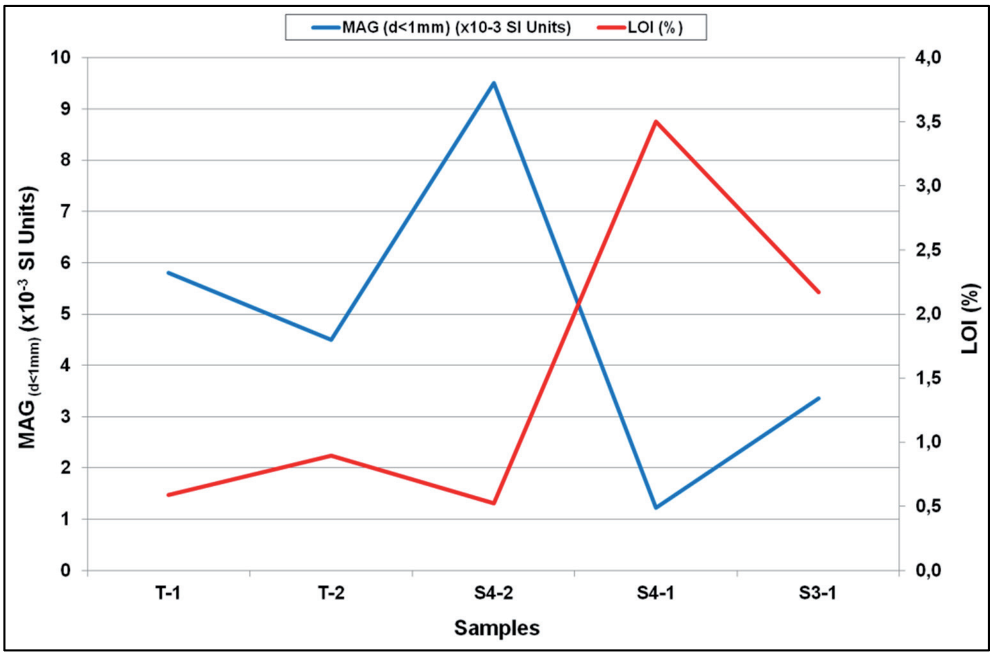


Figure 60 : Magnetic susceptibility (MAG) and loss on ignition (LOI) values of the grab samples

To have a better understanding of LOI-MAG adverse trend, in figure 61 LOI is graphed against MAG. The rock with the highest LOI value (3,50%) has the lowest MAG value ($1,220x10^{-3}$ SI Units) and the lowest quality, whereas the sample with the lowest LOI (0,523%) has the highest MAG ($9,508x10^{-3}$ SI units) and the best quality.

The results of this phase reveal the potential of these parameters for further studies and experiments. The need for additional detailed studies is unavoidable to be able to use these two parameters with a high percentage of success as major indicators for assessing the quality of rocks from desired (various) quarries.

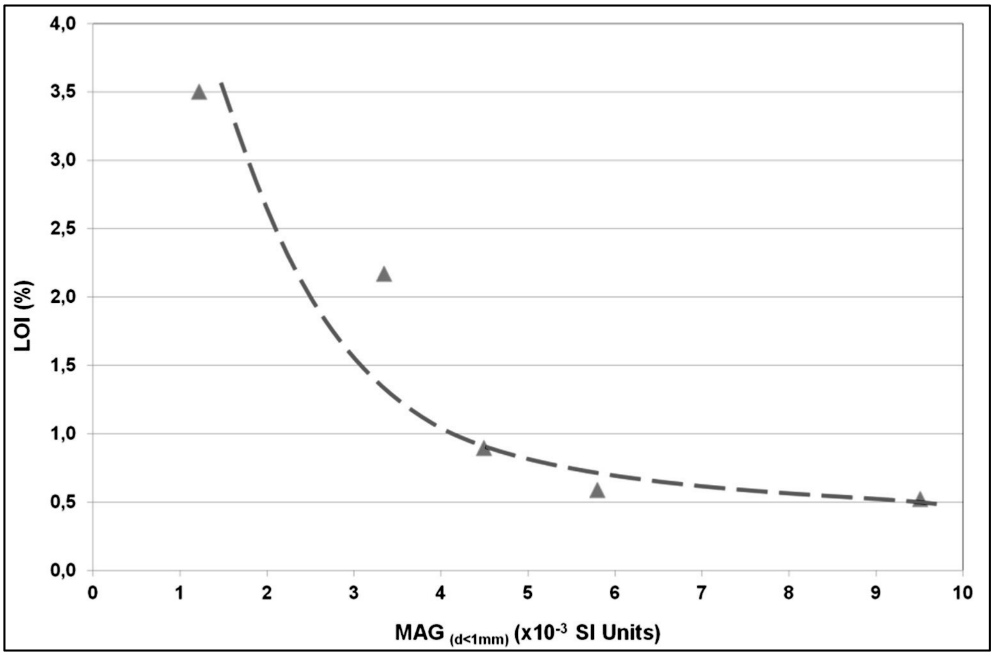


Figure 61 : Loss on ignition (LOI) vs. magnetic susceptibility (MAG) values of the grab samples (the inverse relationship between the two indices is to be noted)

Samples with the least LOI and highest MAG values have shown the best resistance against disintegration, while samples with the highest LOI and lowest MAG values decomposed and fell apart.

In the next phase, we will perform a feasibility study on the possibility of applying LOI and MAG in a wider range. We will also examine the validity of these criteria on a number of additional samples.

6 Feasibility study

According to the preliminary results, we chose two factors, loss on ignition (LOI) and magnetic susceptibility (MAG) as the potential indicators for evaluating the alteration process and consequently the quality of the rocks. The analysis in the reconnaissance study was based on only a small number of samples. Therefore, to be confident about these findings, we studied and analyzed more samples.

6.1 Sampling and their preparation

The quarry´s staff gathered an additional 29 grab samples from different locations within the quarry. The sampling was done in the most appropriate way so that the whole area and all benches of the quarry (with greater concentration on the active benches and in the direction of mine advancing) were covered.

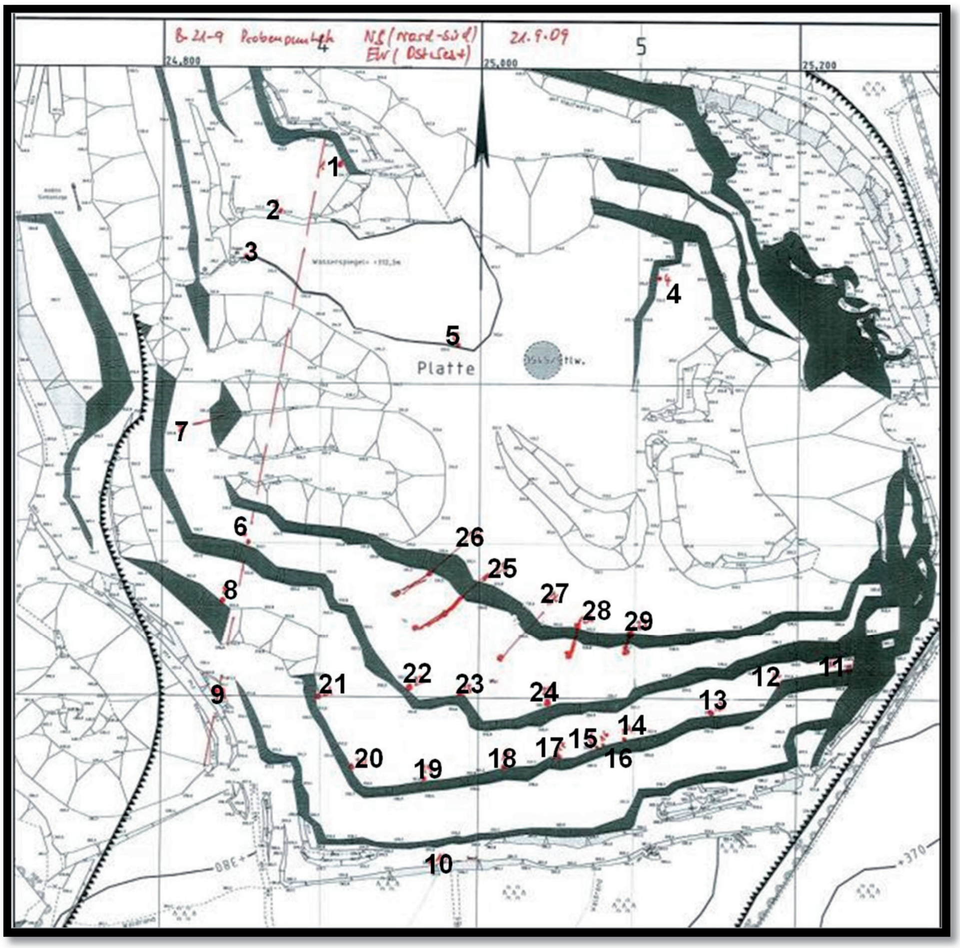


Figure 62 : Location of the grab samples

The 29 samples were all hand-piece samples and were taken to the laboratory for further preparation. Each sample was partially crushed, milled and then sieved through 1mm and 63Mm sieves. The other part of each sample was taken for further possible experiments as well as for reference sample. The prepared samples were then distributed for chemical, microscopic, and magnetic susceptibility evaluations (table 11).

Table 11: Location and sample numbers

Sample No. (TUC)	**Original sample No. (NS : North-South) (EW : East-West)**	**Location in quarry (Bench)**
1	B 21.9-1 NS-S1	1
2	B 21.9-2 NS-S1	1
3	B 21.9-3 NS S1	1
4	B 21.9-4 NS S1	1
5	B 21.9-5 NS S1	1
6	B 21.9-6 NS-S2	2
7	B 21.9-7 NS-S2	2
8	B 21.9-8 NS-S3	3
9	B 21.9-9 NS-S4	4
10	B 21.9-10 NS-S5	5
11	B 21.9-11 EW-S3	3
12	B 21.9-12 EW-S3	3
13	B 21.9-13 EW-S3	3
14	B 21.9-14 EW-S3	3
15	B 21.9-15 EW-S3	3
16	B 21.9-16 EW-S3	3
17	B 21.9-17 EW-S3	3
18	B 21.9-18 EW-S3	3
19	B 21.9-19 EW-S3	3
20	B 21.9-20 EW-S3	3
21	B 21.9-21 EW-S3	3
22	B 21.9-22 EW-S2	2
23	B 21.9-23 EW-S2	2
24	B 21.9-24 EW-S2	2
25	B 21.9-25 EW-S1	1
26	B 21.9-26 EW-S1	1
27	B 21.9-27 EW-S1	1
28	B 21.9-28 EW-S1	1
29	B 21.9-29 EW-S1	1

6.2 Chemical and microscopic analysis

The prepared samples (fraction under 63 µm) were sent for geo-chemical laboratory. A small piece of each rock sample was also sent for microscopic analysis. The results from the chemical and microscopic studies confirmed the first phase studies. Again, the chemical analysis revealed that the LOI variation is in relation with the sodium/potassium/calcium oxide content. The microscopic studies on thin/polished sections also presented the same findings as before: samples with a higher content of magnetite are fresher, where as altered samples have a high content of hematite, which is due to the hydrothermal alteration of magnetite to hematite.

6.3 Loss on ignition measurements

The LOI of the samples was measured by the geo-chemical laboratory (in Canada) for further studies of the samples. Table 12 shows the results of the LOI measurements. The range of alteration in the LOI values is between 1,26% to 3,84%. Table 13 reviews some statistical data of the LOI values.

Table 12 : LOI analysis of the samples

Sample No.	LOI (%)
1	1,39
2	1,76
3	1,46
4	1,32
5	2,05
6	1,59
7	1,56
8	1,88
9	1,26
10	3,17
11	1,26
12	1,35
13	1,90
14	2,57

Sample No.	LOI (%)
15	1,88
16	3,84
17	1,96
18	1,58
19	1,42
20	1,38
21	1,40
22	3,01
23	1,81
24	1,32
25	1,36
26	2,87
27	1,81
28	1,91
29	1,80

Table 13 : Statistics of the LOI measurements

Statistics		
LOI (%)		
N	Valid	29
	Missing	0
Mean		1,8576
Std. Error of Mean		,11965
Median		1,7600
Mode		1,26[a]
Std. Deviation		,64431
Variance		,415
Skewness		1,646
Std. Error of Skewness		,434
Kurtosis		2,366
Std. Error of Kurtosis		,845
Range		2,58
Minimum		1,26
Maximum		3,84
Sum		53,87
Percentiles	25	1,3850
	50	1,7600
	75	1,9350

a. Multiple modes exist. The smallest value is shown

LOI (%)					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	1,26	2	6,9	6,9	6,9
	1,32	2	6,9	6,9	13,8
	1,35	1	3,4	3,4	17,2
	1,36	1	3,4	3,4	20,7
	1,38	1	3,4	3,4	24,1
	1,39	1	3,4	3,4	27,6
	1,40	1	3,4	3,4	31,0
	1,42	1	3,4	3,4	34,5
	1,46	1	3,4	3,4	37,9
	1,56	1	3,4	3,4	41,4
	1,58	1	3,4	3,4	44,8
	1,59	1	3,4	3,4	48,3
	1,76	1	3,4	3,4	51,7
	1,80	1	3,4	3,4	55,2
	1,81	2	6,9	6,9	62,1
	1,88	2	6,9	6,9	69,0
	1,90	1	3,4	3,4	72,4
	1,91	1	3,4	3,4	75,9
	1,96	1	3,4	3,4	79,3
	2,05	1	3,4	3,4	82,8
	2,57	1	3,4	3,4	86,2
	2,87	1	3,4	3,4	89,7
	3,01	1	3,4	3,4	93,1
	3,17	1	3,4	3,4	96,6
	3,84	1	3,4	3,4	100,0
	Total	29	100,0	100,0	

6.4 Magnetic susceptibility measurements

We measured the MAG values on milled-grain size fractions. However, prior to measurements, we defined a proper standard in order to have a constant condition for measuring the MAG values. Based on the defined standard, a plastic container was chosen in order to avoid any impact from the surroundings on the MAG device. The container used was a plastic bucket with a diameter of 13 cm and height of 12 cm (Figure 63). First, we isolated the samples from their surroundings and then we measured the MAG values of the samples. A minimum height of 8 cm of each milled-sample/drill cuttings-sample was placed inside the bucket. The surface of the sample in the bucket was flattened without exerting any power. Any kind of compaction of the sample inside the bucket was avoided. The samples were in a naturally dry state, which is the best condition for this type of testing. The bucket was then placed on a non-metallic surface and the measurements were taken in a non-metallic ambient. In order to obtain the MAG readings, the surface of the hand-device was placed over the flattened surface of the sample in such a way that there was full contact between the two surfaces, but without using any force or pushing the device into the milled sample.

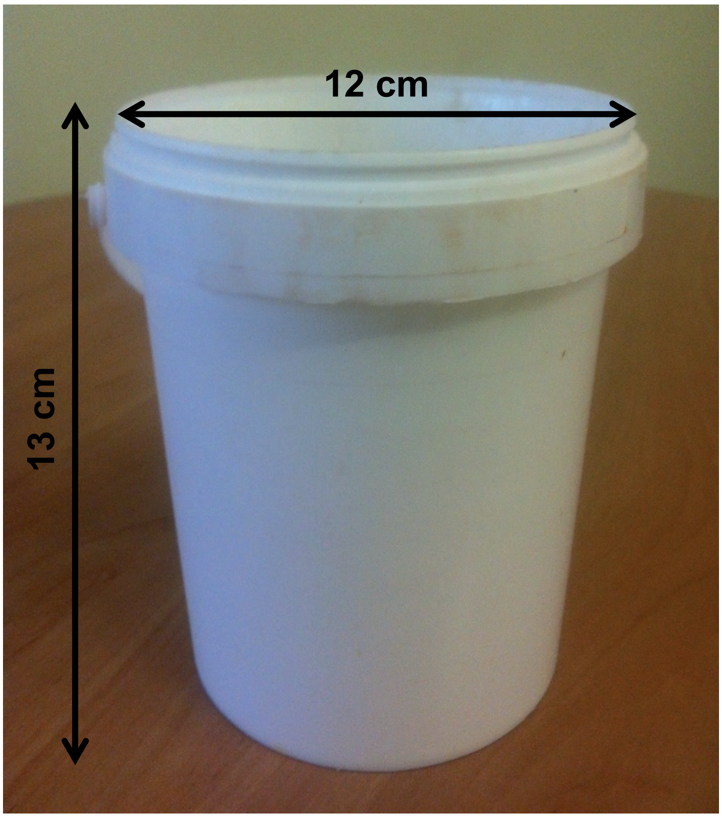


Figure 63 : Defined standard plastic bucket for magnetic susceptibility measurements

In order to carry out the measurements, first we analyzed the effects of different parameters on MAG value. For the milled size category, the following factors were taken into consideration:

- ✓ Moisture: moisture and water content have no significant effect on the measurements. However, it is better to have a fairly dry, though not oven dried sample; air-drying is sufficient for this process. If the samples are so wet that they are compacted to each other (solidified and concreted, in case of minerals with high clay content), then the measurements could be affected. As a result, the samples should not be overly wet and cohesive, and if it is, then it should be dried to gain the type of powder or loose format explained above.

- ✓ Compaction: the degree of compaction is important and has impact on the results. The more compacted the material, the higher the MAG value. This is because when materials are less compacted, there are greater air gaps between particles. Since the manufacturers set the MAG value for open air to zero (minimum MAG value), air gaps cause a decrease in the MAG value. When the sample is compacted, the number of air voids between the particles decrease and the MAG value will increase. That is why the importance of not compacting the samples was mentioned in the previous section. It is enough to put the powder sample in the bucket and then start reading over a flat surface.

- ✓ Surface area: in order to obtain accurate measurements, the surface area of the device must be covered by material. The surface of the material must be even and flat in order to create the best contact with the device surface. Reading on undulating, half-flattened, or incomplete surfaces leads to errors in the readings.

- ✓ Thickness: the thickness of the material under the surface of the device has an impact on the readings. A suitable depth is about 8 cm. Having too low a thickness, results in lower measured values. Having a greater thickness, more than 8 cm, does not influence the readings because the scan depth (penetration depth) limitation of the equipment is approximately 8 cm.

- ✓ Grain size: the grain size of a sample has an effect on the readings, as well. As the grains increase in size, the MAG value decreases, and as the grain size decreases, the MAG value increases. If a rock sample is large enough to cover the entire surface of the device, however, this rule no longer holds true. For example, the reading obtained from a 1mm sized sample gives a higher MAG value than a 5 mm sample. In the case of a mixed sample (e.g. drilling fines or drill cuttings), where there is a mixture of grains ranging in size from micrometers to millimeters, the MAG result will be higher. In the case of a homogenous sample with a particulate size of 4 cm to 5 cm, there is air void between the particles and low MAG values are obtained. However, with a sample that is a mixture of grain sizes, namely from 0 cm to 5 cm, the void between the larger particles is filled by the smaller particles, thereby increasing the MAG value. In the case of a large rock sample, the value will reach its highest point, since the rock is a fully compacted medium. The MAG value of a rock is always greater than the value of its powdered form. Figure 64 shows the effect of grain size on the MAG values. This is an example to display the effect of the particle size on MAG value (regarding figure 64 we have to mention that we made the readings on the rock-milled samples from this specific quarry and this graph is not a universal graph). For each quarry and each grain size, the correlation graph should be produced separately based on the requirements and needs.

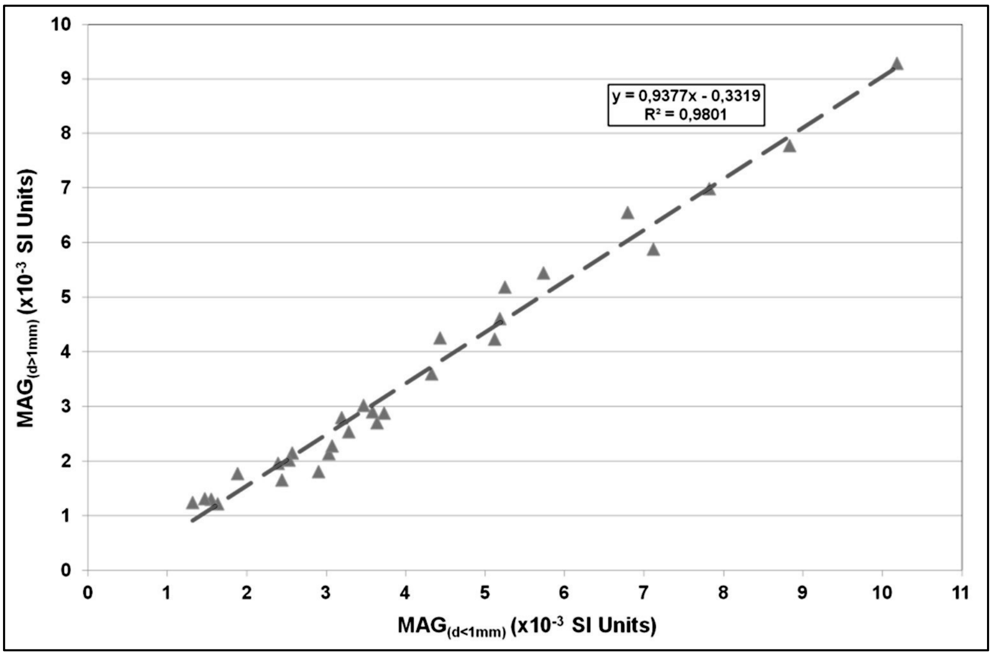


Figure 64 : MAG values for two different size categories; under 1mm and over 1mm (correlation graph)

- ✓ Reproducibility of the measurements: the results are highly reproducible. We performed thousands of measurements on both milled samples (as well as drilling fines) and rock surfaces and as a result, the readings are easily reproducible. The 1-sigma (1σ) error margin was less than five percent.

Based on the standard definition and aforementioned restrictions, the 29 samples were prepared and the under 1 mm particulate was separated for MAG measurements. We measured the MAG values of the milled samples by the KT-10 hand-held magnetic susceptibility device. As before, we performed at least ten readings on each sample and the averaged value was taken as its MAG value. The results of the measurements are in table 14. The range of variation of MAG values lies between 1,32 (x10^{-3} SI Units) and 10,18 (x10^{-3} SI Units).

Table 14 : MAG values measured on under 1mm powder samples

Sample No.	$MAG_{(d<1mm)}$(x10^{-3} SI Units)
1	3,19
2	2,44
3	3,47
4	5,12
5	2,57
6	4,33
7	2,90
8	4,43
9	10,18
10	1,63
11	8,83
12	5,18
13	5,25
14	1,55

Sample No.	$MAG_{(d<1mm)}$(x10^{-3} SI Units)
15	2,39
16	1,32
17	3,03
18	5,73
19	3,64
20	7,12
21	3,28
22	1,47
23	1,88
24	3,58
25	7,82
26	3,07
27	6,79
28	3,73
29	2,53

The MAG measurements were carried out on particulate over 1mm in size as well. The correlation graph between the two-grain sizes can be seen in figure 64. As explained above, the values measured for milled rocks above 1mm in size were lower due to the existence of more air voids between the bigger particles. Table 15 shows the statistical data of the MAG measurements.

Table 15 : Statistical data of MAG measurements

Statistics		
$MAG_{(d<1mm)}(x10^{-3}$ SI Units)		
N	Valid	29
	Missing	0
Mean		4,084483
Std. Error of Mean		,4221396
Median		3,470000
Mode		1,3200[a]
Std. Deviation		2,2732915
Variance		5,168
Skewness		1,106
Std. Error of		,434
Kurtosis		,745
Std. Error of Kurtosis		,845
Range		8,8600
Minimum		1,3200
Maximum		10,1800
Sum		118,4500
Percentiles	25	2,485000
	50	3,470000
	75	5,215000

a. Multiple modes exist. The smallest value is shown

$MAG_{(d<1mm)}(x10^{-3}$ SI Units)					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	1,32	1	3,4	3,4	3,4
	1,47	1	3,4	3,4	6,9
	1,55	1	3,4	3,4	10,3
	1,63	1	3,4	3,4	13,8
	1,88	1	3,4	3,4	17,2
	2,39	1	3,4	3,4	20,7
	2,44	1	3,4	3,4	24,1
	2,53	1	3,4	3,4	27,6
	2,57	1	3,4	3,4	31,0
	2,90	1	3,4	3,4	34,5
	3,03	1	3,4	3,4	37,9
	3,07	1	3,4	3,4	41,4
	3,19	1	3,4	3,4	44,8
	3,28	1	3,4	3,4	48,3
	3,47	1	3,4	3,4	51,7
	3,58	1	3,4	3,4	55,2
	3,64	1	3,4	3,4	58,6
	3,73	1	3,4	3,4	62,1
	4,33	1	3,4	3,4	65,5
	4,43	1	3,4	3,4	69,0
	5,12	1	3,4	3,4	72,4
	5,18	1	3,4	3,4	75,9
	5,25	1	3,4	3,4	79,3
	5,73	1	3,4	3,4	82,8
	6,79	1	3,4	3,4	86,2
	7,12	1	3,4	3,4	89,7
	7,82	1	3,4	3,4	93,1
	8,83	1	3,4	3,4	96,6
	10,18	1	3,4	3,4	100,0
	Total	29	100,0	100,0	

6.5 Reference tests

To be able to evaluate the results of MAG and LOI measurements, a reference test was chosen. Prior to our studies, the company has always applied the following two methods to assess the quality of aggregates from their quarries:

- ✓ Ethylene glycol test
- ✓ Methylene blue dye test

As explained before, these tests do not provide a high degree of accuracy; the glycol test gives the result of the reaction of rock minerals with ethylene glycol and the methelyne blue test is used for the detection of clay minerals. This means that a rock might be instinctually weak, however due to its chemistry, it does not react with glycol or methylene blue. In another word, although the rock is weak, no reaction takes place and the results of the experiments are perfect, giving a false result. In these experiments, it frequently occurs that both tests reflect a negative result, meaning the rock is not durable and will easily break down, or one returns negative result while the other one gives a positive result or that both give positive results, however, the results prove to be false. Therefore, there is a very weak correlation between these two methods and rock quality.

For the last decade, the company was analyzing their quarry rock using these two methods, but they still had to pay compensation on their products. They obtained positive results on a product and thinking they had a good quality product, they sold it, but soon the rocks were degraded and disintegrated. Because of these unreliable tests, many companies and their buyers have doubts about the quality of the products. Other problems regarding these two methods of testing are long sampling (preparation) times, low reproducibility of the results, not true representation of the quarry rock, and they are only applicable on hand-pieces. A detailed description of these methods was provided in the third chapter of this work.

In this stage, to evaluate and assess the obtained results of the LOI and MAG experiments, we chose a reference test. With respect to this issue, the samples (in hand-piece form) also underwent the glycol test. The results of the glycol test on the 29 samples are shown in table 16. The glycol test is expressed in weight loss percentage of the sample after exposure to the glycol. The statistical data regarding the glycol testing is shown in table 17.

Table 16 : Results of the glycol test on hand-piece samples

Sample No.	Glycol test (%)
1	0,24
2	-0,64
3	0,66
4	0,07
5	33,09
6	10,21
7	1,89
8	4,22
9	0,99
10	69,9
11	1,35
12	0,38
13	7,24
14	69,7

Sample No.	Glycol test (%)
15	1,71
16	2,49
17	0,51
18	0,22
19	0,27
20	0,17
21	0,60
22	64,7
23	0,33
24	0,14
25	0,07
26	20,05
27	0,13
28	4,93
29	0,71

The range of the glycol test results is from -0,64 to 69,9 percent. A special remark on the cause of the negative percentage: the negative value may have been caused by experimental failure and errors or by $Mg(OH)_2$ precipitation. $Mg(OH)_2$ precipitation can occur at the end of the glycol test, when the samples start to cool down and dry. At that time, the temperature, pressure and pH of the medium changes, and this change may cause some materials such as $Mg(OH)_2$ and SiO_2 to precipitate inside the air voids, spaces, and cracks of the samples, leading to a greater final weight [11]. For the purposes of the study, we regarded negative values as zero percentage weight loss, or no change.

Table 17 : Statistical data of the glycol test

Statistics		
Glycol test (%)		
N	Valid	29
	Missing	0
Mean		10,2403
Std. Error of Mean		3,93957
Median		,7100
Mode		,07
Std. Deviation		21,21523
Variance		450,086
Skewness		2,325
Std. Error of Skewness		,434
Kurtosis		4,171
Std. Error of Kurtosis		,845
Range		69,90
Minimum		,00
Maximum		69,90
Sum		296,97
Percentiles	25	,2300
	50	,7100
	75	6,0850

Glycol test (%)					
		Frequency	Percent	Valid Percent	Cumulative Percent
Valid	0	1	3,4	3,4	3,45
	0,07	2	6,9	6,9	10,34
	0,13	1	3,4	3,4	13,79
	0,14	1	3,4	3,4	17,24
	0,17	1	3,4	3,4	20,69
	0,22	1	3,4	3,4	24,14
	0,24	1	3,4	3,4	27,59
	0,27	1	3,4	3,4	31,03
	0,33	1	3,4	3,4	34,48
	0,38	1	3,4	3,4	37,93
	0,51	1	3,4	3,4	41,38
	0,60	1	3,4	3,4	44,83
	0,66	1	3,4	3,4	48,28
	0,71	1	3,4	3,4	51,72
	0,99	1	3,4	3,4	55,17
	1,35	1	3,4	3,4	58,62
	1,71	1	3,4	3,4	62,07
	1,89	1	3,4	3,4	65,52
	2,49	1	3,4	3,4	68,97
	4,22	1	3,4	3,4	72,41
	4,93	1	3,4	3,4	75,86
	7,24	1	3,4	3,4	79,31
	10,21	1	3,4	3,4	82,76
	20,05	1	3,4	3,4	86,21
	33,09	1	3,4	3,4	89,66
	64,70	1	3,4	3,4	93,10
	69,70	1	3,4	3,4	96,55
	69,90	1	3,4	3,4	100,00
	Total	29	100,0	100,0	

6.6 Results and discussions

As stated above, we applied the ethylene glycol test in order to evaluate the two recognized quality control criteria: LOI and MAG. The results of all three measurements are shown in table 18.

Table 18 : Results of MAG, LOI, and glycol testing in comparison with one another

Sample No.	$MAG_{(d<1mm)}$($x10^{-3}$ SI Units)	LOI (%)	Glycol test (%)
1	3,19	1,39	0,24
2	2,44	1,76	0
3	3,47	1,46	0,66
4	5,12	1,32	0,07
5	2,57	2,05	33,09
6	4,33	1,59	10,21
7	2,90	1,56	1,89
8	4,43	1,88	4,22
9	10,18	1,26	0,99
10	1,63	3,17	69,9
11	8,83	1,26	1,35
12	5,18	1,35	0,38
13	5,25	1,90	7,24
14	1,55	2,57	69,7
15	2,39	1,88	1,71
16	1,32	3,84	2,49
17	3,03	1,96	0,51
18	5,73	1,58	0,22
19	3,64	1,42	0,27
20	7,12	1,38	0,17
21	3,28	1,40	0,60
22	1,47	3,01	64,7
23	1,88	1,81	0,33
24	3,58	1,32	0,14
25	7,82	1,36	0,07
26	3,07	2,87	20,05
27	6,79	1,81	0,13
28	3,73	1,91	4,93
29	2,53	1,80	0,71

In the following sections, in order to deepen our assessments, we have compared each two parameters to one another separately. At the end, we have also defined a “threshold” of detection for each of the factors.

6.6.1 LOI vs. glycol test

The company applies a limit of 10% on the glycol test. This means that a loss of up to 10% is acceptable and anything above is regarded as inadequate rock quality. Using table 18 as a reference, this quality limit can be used to see further correlations in the data. All of the samples that had a glycol test result greater than 10% also had a LOI value of more than 2%, which means that the error percentage of the glycol test, when larger than 10%, was zero. Out of the remaining samples, those with glycol test values less than 10%, only one, (sample No. 16) had a LOI value that did not correctly correspond, meaning that the error rate of the test when below 10% is about 3%.
Given the data collected and the explanation above, a LOI limit of 2% will be used for LOI measurements; rocks with an average LOI greater than 2% can be regarded as low-quality rocks while an average LOI of less than 2% can be considered good-quality rocks.
Regarding the glycol test experiments and its limit, a couple of point shall be mentioned here:

- ✓ The glycol test limit is a rock-type dependent value and is not a universal rule. In some cases, it can be defined by the responsible authorities and be set as low as 2%. In the case of this quarry, the hand-piece samples were further analyzed after the glycol test. The rocks having a weight loss of less than 10% had not disintegrated or broken down. In most of them, only the edges of the rock were broken or chipped, in others, materials from the spacings and joints were washed out, and in some cases, the damage was done prior to the experiment, in the blasting process. Based on these findings, the limit for the glycol test as a rock quality index in the quarry is assumed to be around 10%. Figure 65, found below, is used as an example to display this issue. The other samples that had glycol test values of less than 10%, showed the same results. The most important point is that the thin/polished section microscopic studies revealed this correlation and corresponded largely with the LOI and MAG values (figure 66).

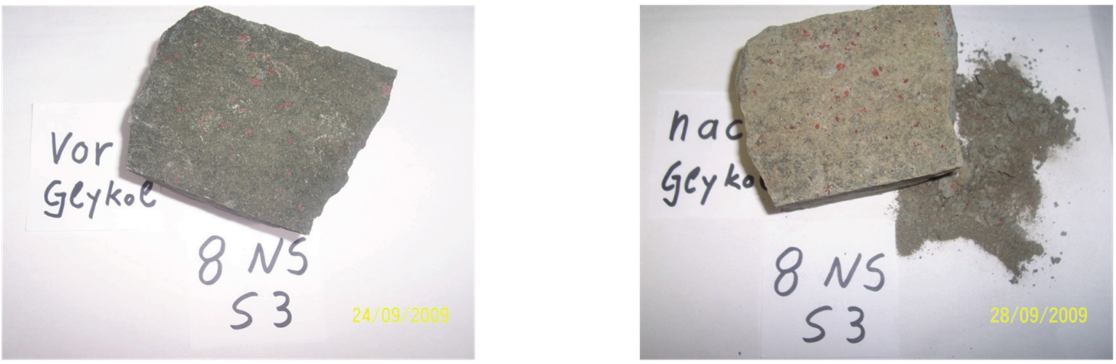


Figure 65 : Rock sample No. 8 before (left) and after (right) glycol test (glycol test=4,22%, LOI=1,88%, MAG=4,43x10^{-3} SI Units)

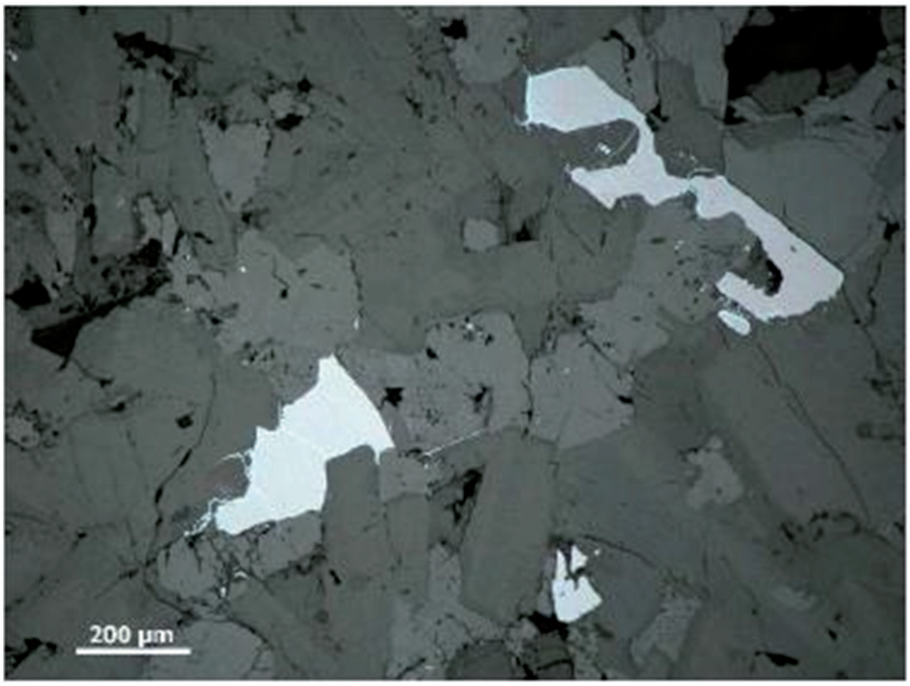


Figure 66 : Microscopic photo of sample No. 8 showing low alteration (low magnetite alteration)

- ✓ Sample No. 6 has a glycol test value of 10,21%. Analysis of the photos of this sample before and after the glycol experiment showed that this rock sample was also not disintegrated and though a corner piece of the sample was broken, in fact this breakage was the result of the cracks developed by blasting (figure 67). Microscopic studies also confirmed a low alteration feature for this sample, which was in accordance with the LOI and MAG results (figure 68). Due to the limited disintegration, and because 10.21% was moderately close to the limit, it was regarded as being a part of the under 10% category and as having a good quality.

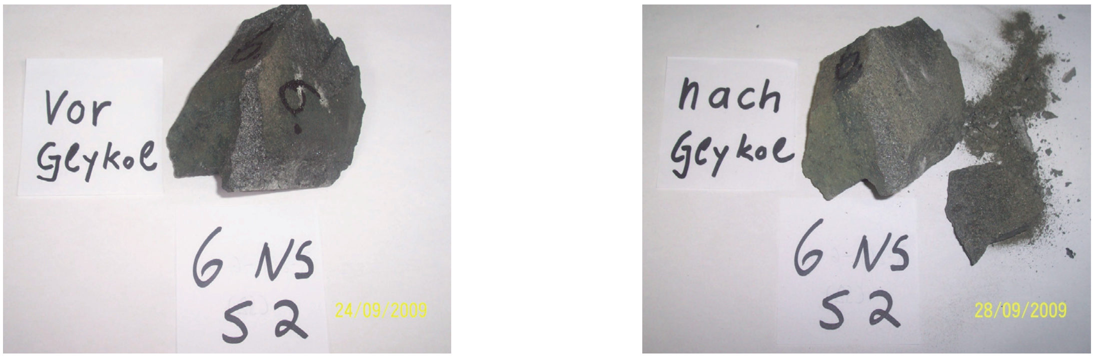


Figure 67 : Sample No. 6, before (left) and after (right) glycol test (glycol test= 10,21%, LOI=1,59%, MAG= 4,33x10-3 SI Units)

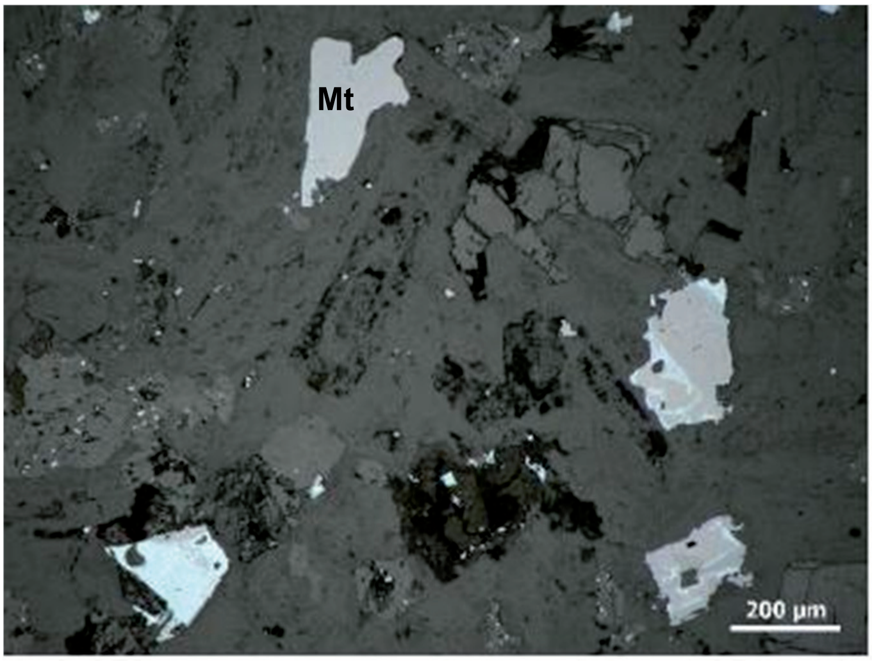


Figure 68 : Microscopic thin/polished section view of sample No. 6 (low magnetite alteration, Mt=magnetite)

- ✓ Regarding sample No. 16, it shall be noted that, this sample had a LOI value of 3,84%, meaning that, based on LOI results, it was a poor quality rock while according to glycol test (2,49%), it was a good quality rock. In this case, the LOI limit would have caused the rock sample to be discarded from the production cycle instead of being sent to the crushing plant and then on to be used as part of a railway ballast. However, based on the glycol test, there was no problem with this rock and it should have been sent on to be processed further and then used in railway applications. Microscopic studies also correlated well with LOI result. In such an instance, the glycol test has failed in accurately assessing the quality of the rock, which leads to additional costs to the company.

- ✓ Due to these ramifications, a solution was an important area of focus in order to allow the company to work with more confidence in their rock quality. One option is to sell these rocks (those with conflicting analyses and uncertain quality), for purposes other than railway ballasts, such as concrete applications.

- ✓ Among all 29 samples, there was no single sample that was recognized as poor quality by the glycol test but determined to be high quality by the LOI experiment. All the samples that were shown to be poor quality samples by the glycol test were also grouped as low quality rocks by LOI factor.

Applying the limits of 10% for glycol testing and 2% for LOI to the statistical evaluations provided in tables 13 and 17, shows that about 83% of the samples were categorized as good quality rocks (table 13).

6.6.2 MAG vs. glycol test

Table 18 also shows the experimental values that we gathered by MAG and glycol tests. The comparison shows that all samples that have a glycol test value of more than 10%, had a MAG value of less than about $3{,}00 \times 10^{-3}$ SI Units. This means all the samples that were recognized as low quality samples by the glycol test, were also shown to be low quality samples by the MAG experiment. On the other hand, there were four samples that had glycol test values below 10% (good quality rocks), but still had a MAG value of less than $3{,}00 \times 10^{-3}$ SI Units (there was about 13% error). These samples were numbers 2, 15, 23, and 29. As explained before, even if the MAG results are in error and the company takes proper actions based on MAG results, the company will not lose anything and they have a higher confidence margin. If the results of glycol tests are not reliably accurate, and the material is sold and then begins to degrade, the company will have a large problem on their hands. As previously mentioned, in this case, it is better to sell these types of materials for purposes other than railway ballasts.

Based on this research, the limit of detection for MAG at this stage is about $3,00x10^{-3}$ SI Units, although further experiments are needed to prove it.

6.6.3 MAG vs. LOI

The two new criteria used in evaluation of the alteration extent of rock samples and consequently the quality of the rocks in this section were LOI and MAG. The LOI and MAG values that resulted from this phase of studies confirmed the first phase of studies; the higher the LOI, the higher the degree of alteration and the lower the MAG value, consequently leading to a poorer quality of rock. LOI and MAG have an inverse relationship with one another and the increase of one parameter leads to the decrease of the other. Figures 69 and 70 depict this relation again.

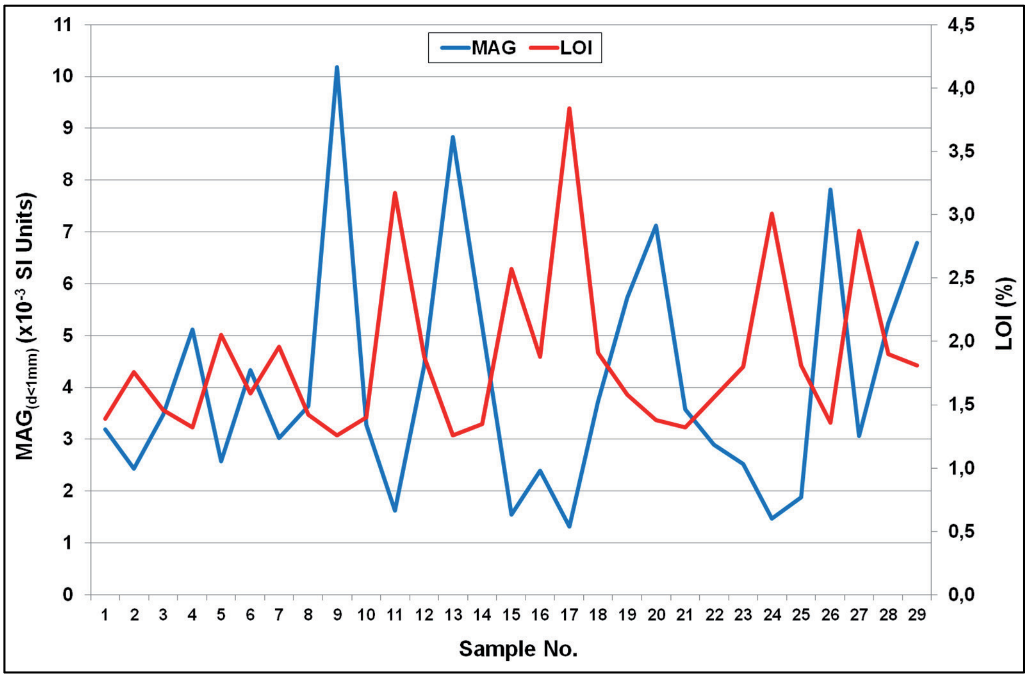


Figure 69 : Comparison between LOI and MAG values of the samples

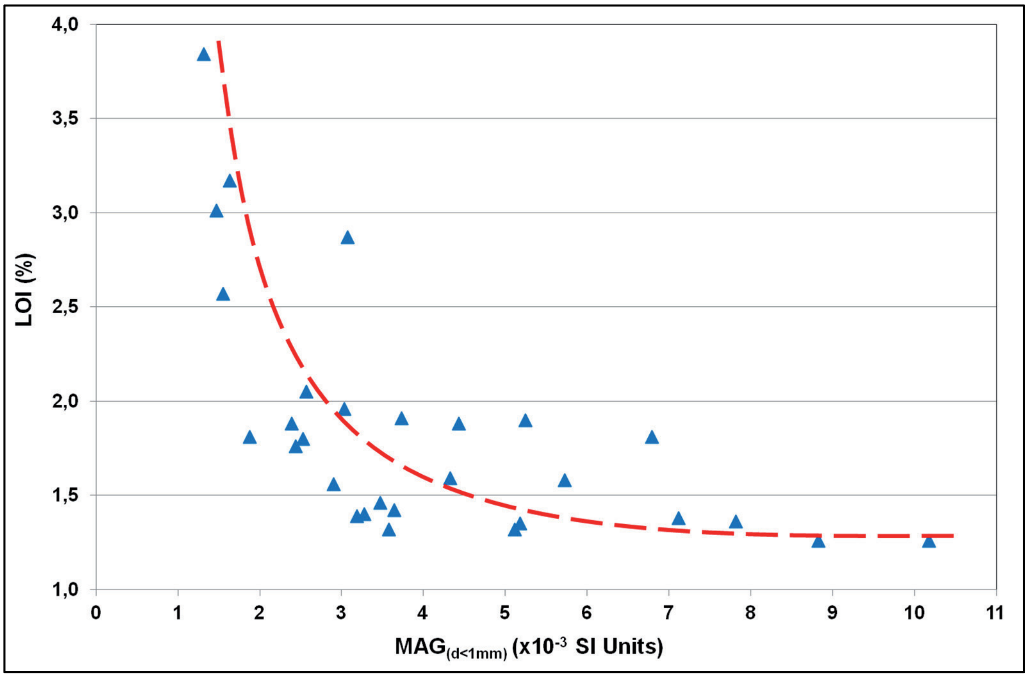
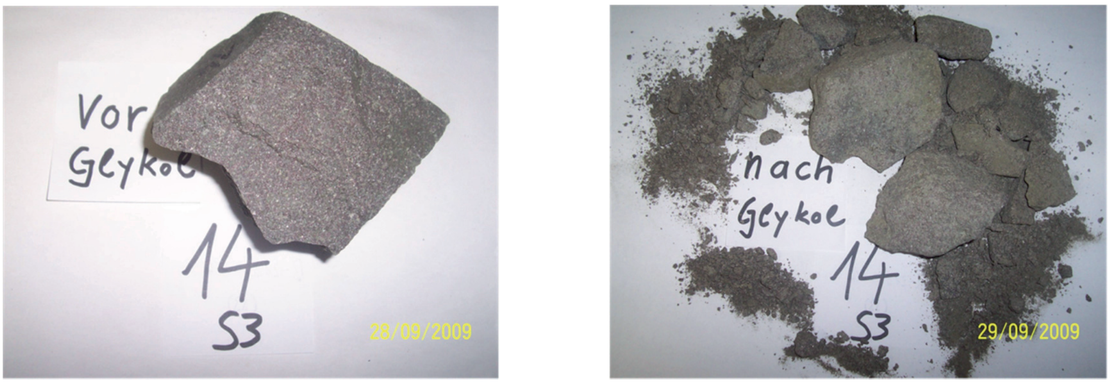


Figure 70 : Loss on ignition vs. magnetic susceptibility of the samples

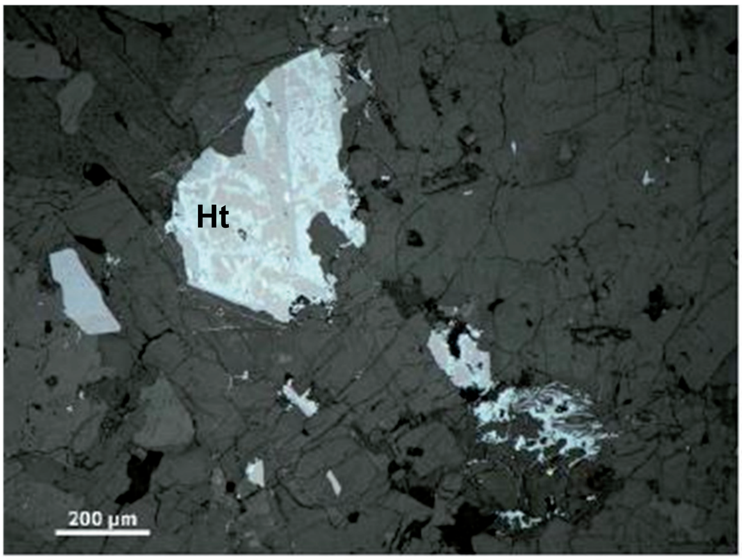
The microscopic studies of the samples also confirm the good correlation between the LOI and MAG values.

We used glycol test as a reference test to evaluate the LOI and MAG values and then define a limit of detection value for each to measure the quality of rocks. Based on the assessments, a LOI value of 2% and MAG of $3{,}00 \times 10^{-3}$ SI Units are good cutoff points. This means that rock samples having LOI values of less than 2% and MAG values higher than $3{,}00 \times 10^{-3}$ SI Units have a low alteration degree and thus maintain a higher quality through time.

Figures 71 and 72 show additional photos from the glycol testing and their corresponding MAG and LOI values as well as their microscopic this/polished section photos.

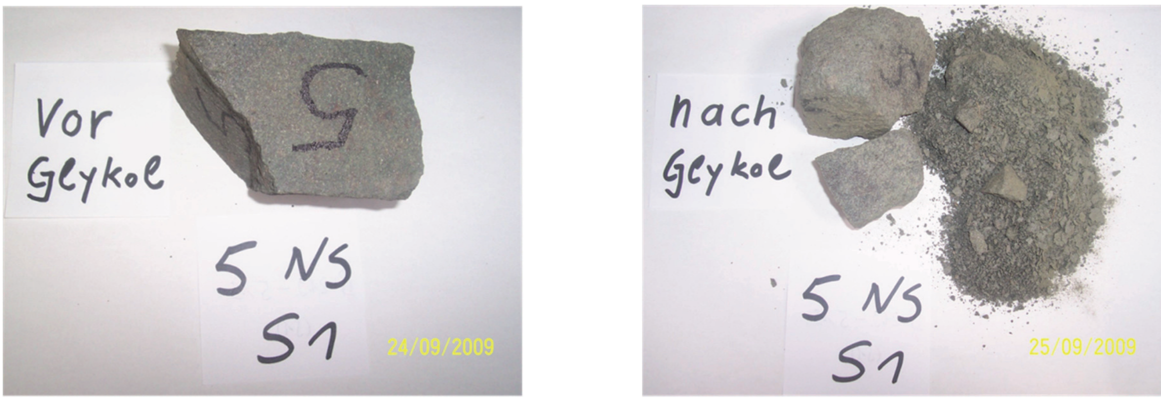


(a)

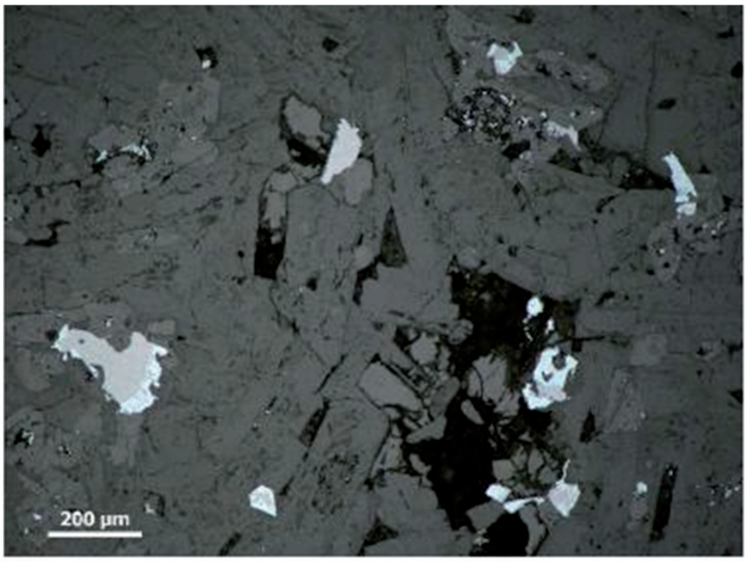


(b)

Figure 71 : Sample No. 14, (a) before (left) and after (right) glycol test. The sample is completely disintegrated after the glycol test (glycol= 69,7%, LOI=2,57% and MAG= 1,55x10^{-3} SI Units). (b) The microscopic section also shows high alteration of the sample (Ht=Hematite)



(a)



(b)

Figure 72 : Sample No. 5, (a) before (left) and after (right) glycol test. The sample is completely disintegrated after the glycol test (glycol= 33,09%, LOI=2,05% and MAG= $2{,}57 \times 10^{-3}$ SI Units). (b) The microscopic study also shows a high degree of alteration

As a final result of this phase, we deduced that between the LOI and MAG of a sample, the MAG value is likely a better suited parameter for quality assessment purposes because,

1- MAG measurements require a hand-held device. Therefore, this method has the potential to be directly carried out in the field.

2- It is a quick, reliable, economic, and reproducible method of testing.

3- It covers a wide range of variation, starting from zero and going to large numbers, such as 30×10^{-3} SI Units. Therefore, grouping rocks using this factor is easier than LOI. Variation of LOI has a limited range, e.g., from 0% to a maximum of 10% in this case.

4- It is very applicable to both rock samples as well as powder samples, and provides consistent results with either form.

To use the MAG value as the main criteria for distinguishing rock durability and quality, further measurements and experiments are required to make sure MAG is accurate. However, in special cases as will be discussed later, LOI measurements are also inevitable. In next phase, a more detailed study is carried out with respect to MAG and LOI measurements.

7 Detailed studies

As a result of the last section, the samples that were disintegrated in the glycol test, with weight loss of more than 10%, had LOI value of higher than ca. 2% and a magnetic susceptibility of less than ca. $3,00 \times 10^{-3}$ SI Units. The aim of this phase is to check this reverse relation between the selected quality factors, and to make sure that magnetic susceptibility is the right choice for real-time recognition of rock durability and thirdly determine the limit of detection with a higher degree of confidence.

To satisfy this goal, we managed a detailed study program consisting of field measurements and laboratory measurements. For each stage a wide sampling and experimental program was scheduled to hand in the most exact results. The MAG measurements were carried out using a hand-held magnetic susceptibility device (KT-10) and the LOI test were done by a laboratory muffle oven.

7.1 Field experiments

The major goals of performing field studies were to:

1- Check the transferability of the methods (LOI and MAG) and their corresponding devices to field operations.
2- Perform analytical and statistical analysis of the measurements in order to confirm the limits of detections.
3- Check the scale-up feasibility, which means examining the possibility of the desired methods and their detection limits to be scaled up from laboratory scale to field scale (practical daily operation).
4- Control the reproducibility of the results.
5- Carry out analytical and statistical evaluation of data to find out the quality distribution in the quarry and create a three dimensional quality model for the quarry.

To increase the certainty of the field results, the field measurements were examined by means of drilling boreholes. In fact, the main aim of drilling the boreholes in different locations of the quarry was to:

1- Check the reproducibility of the results in the field operations
2- Control the relationship between the quality factors (LOI and MAG)

3- Select a better, more reliable, and more secure quality factor for real-time recognition of rock quality

The field experiments consisted of two parts, the field measurements, and the complementary lab measurements.

7.1.1 Field measurements

7.1.1.1 Quarry wall measurements and the corresponding results

In this stage, the magnetic susceptibility of the whole quarry was measured in centimeter intervals with the use of a magnetic susceptibility hand device (KT-10). The distances between measurements were between 10 cm to a maximum of 1 m, which was a function of assumed changes in rock mineralogy, lithology, tectonics, and sometimes color of the rocks. The frequency of measurements close to the faulted zones, crushed zones, altered regions and locations under more tectonic pressures, was higher. In total about 5000 single measurements from 1530 locations were performed on the wall of the quarry benches. For each location, the MAG value was measured several times and then an average value was given to that location. At the same time of the measurements, the co-ordinate (X and Y) of the locations was also read by the use of a GPS hand-held device (Garmin GPS). With this method, the MAG values with their respective locations could be mapped on the quarry map AutoCad file in order to build up a magnetic susceptibility 3-D model of the quarry. Figure 73 shows a schematic view of the MAG measurements on the walls.

Figure 73 : Field measurements of MAG on the wall of the quarry

The results of the measurements may be seen in figure 74. This figure shows the cumulative percentage of the MAG measurements in the whole quarry. Assuming the limit of detection for MAG to be 3,00x10^{-3} SI Units (as determined before), about 20% of the whole quarry will be categorized as low quality rock.

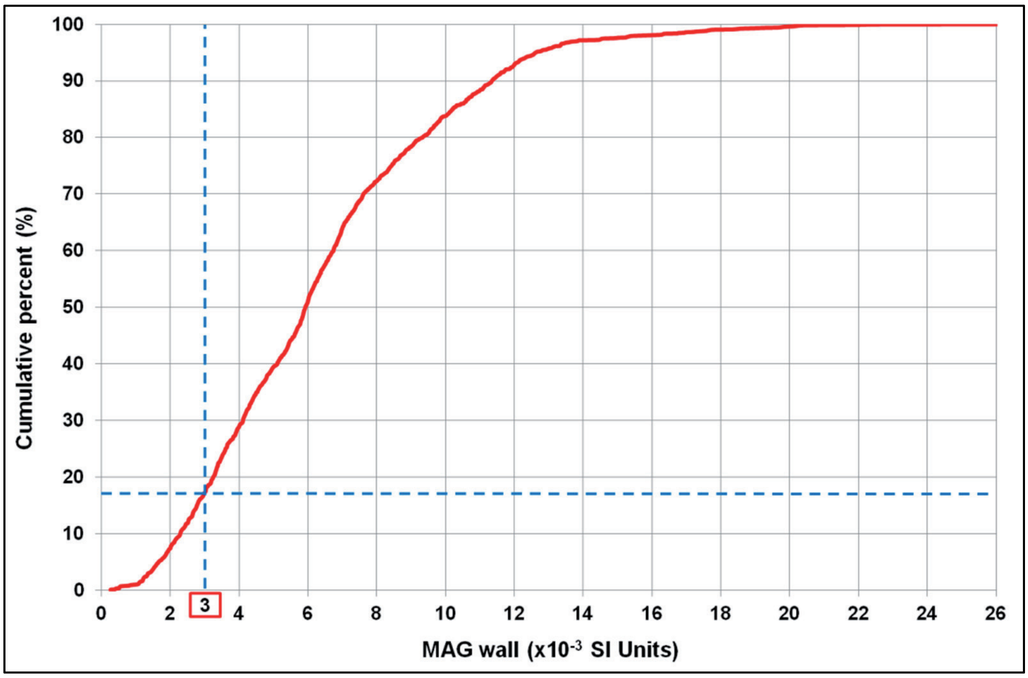


Figure 74 : Cumulative percentage of MAG values of the quarry. More than 5000 measurements on 1543 locations were taken from wall of the quarry.

7.1.1.2 Laboratory measurements and the corresponding results

During the measurements of MAG values in the quarry, everywhere that there was a sharp change in MAG value or realized that there might be any kind of change in the quality of the rock (resulted from change in mineralogy, alteration, etc.) a hand piece rock sample was also taken. The grab samples were sent to the laboratory and their MAG and LOI values were measured. As a result, a total number of 152 grab samples were gathered and analyzed for their MAG and LOI values. The MAG measurements were carried out on the largest flat surface of each sample, in a way that the surface of the rock covered the complete surface of the MAG device (KT-10). At least ten readings (possibly from different sides) were performed on each sample and then the average value was taken as the MAG value of the sample. Then they were prepared for the LOI experiments, which means they were crushed, milled, sieved, and then de-moisturized in an oven for 24 hours under 100°C to 105°C. For LOI tests, each sample was weighed and put in a crucible, then placed in muffle oven, and finally heated up to

850°C for two hours. For every sample, at least three distinct LOI values were measured and then averaged. It shall be noted that for each particular sample, incase each of the three results were out of range or assumed to be false, the experiment was carried out again in order to minimize the laboratory errors. Therefore, for 152 hand piece samples of this phase, at least 1520 single MAG measurements and 456 single LOI values were obtained. Increasing the number of experiments and sampling population helped us to overcome the possible failure in different phases of studies such as sampling, preparation, experiments, analyzing and so on.

Figures below show the results of these measurements. As it is clear in figures 75 and 76, the inverse relationship between the MAG and LOI values is confirmed here as well. Increase of one factor leads to the decrease of the other one.

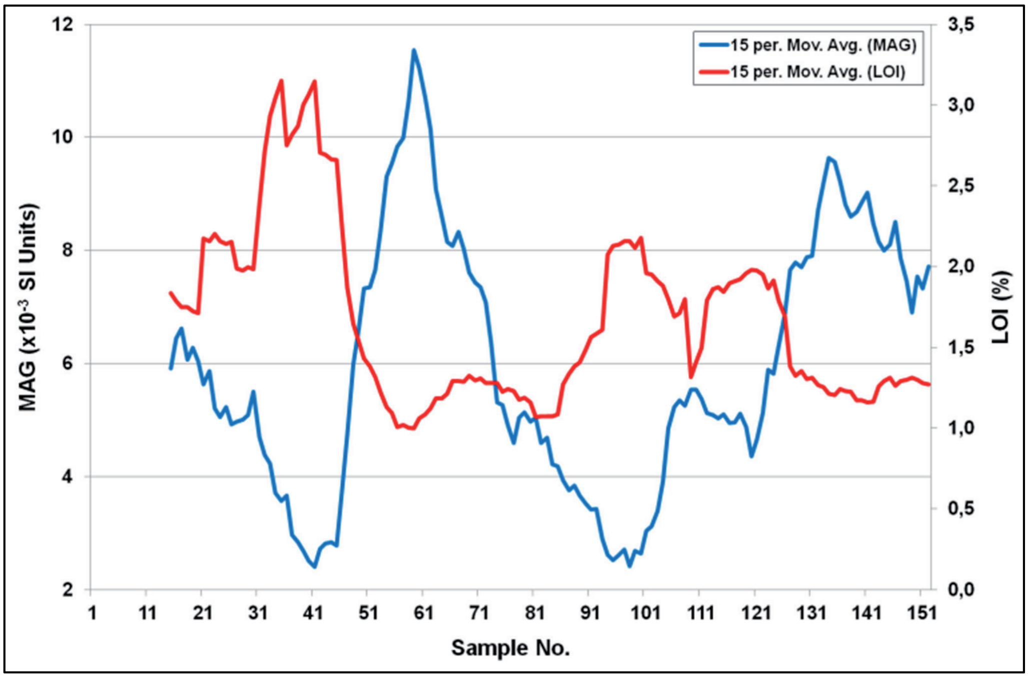


Figure 75 : Inverse relationship between the MAG and LOI values of the 152 hand piece samples

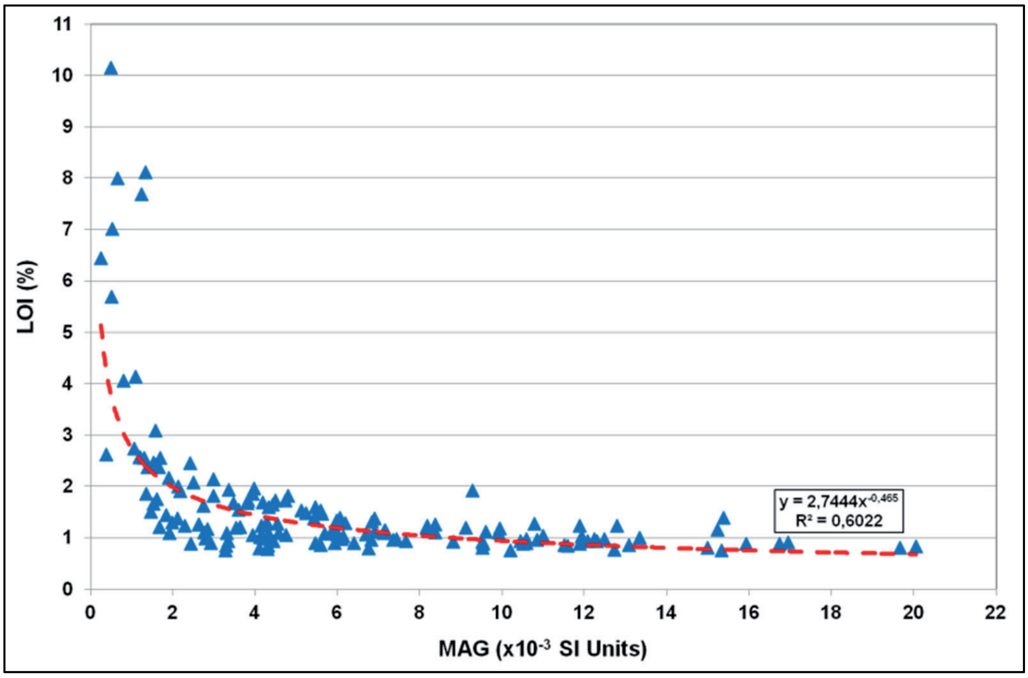


Figure 76 : Relationship between the MAG and LOI values of the 152 hand-piece samples

Figures 77 and 78 depict analysis of the overall distribution of MAG and LOI in the quarry. As shown in the graphs, the pre-determined limits for LOI and MAG (a LOI value of 2% and magnetic susceptibility of 3,00x10^{-3} SI Units) are also confirmed here. Assuming this limit of detection as the basis, about 20% of the quarry materials have a low quality and are not appropriate for railway ballast applications (this result was also obtained in the feasibility studies). The same result was also gained from the MAG measurements of the walls. Due to this result, the 20% of low quality materials must not be sold for railway ballast applications.

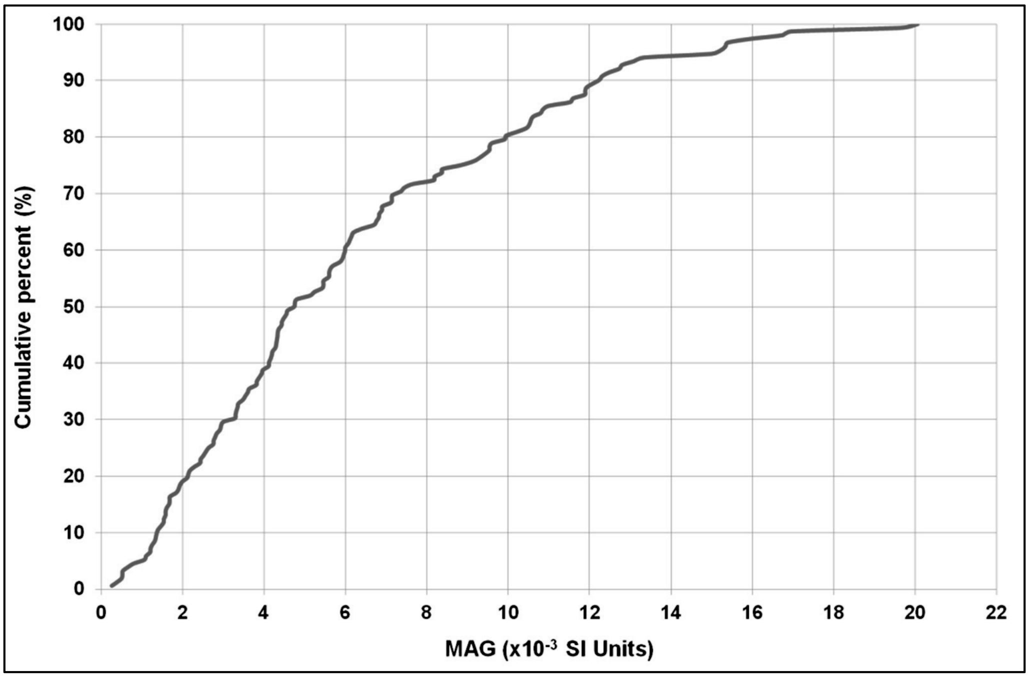


Figure 77 : Cumulative percentage of MAG values (measured on 152 hand-piece samples)

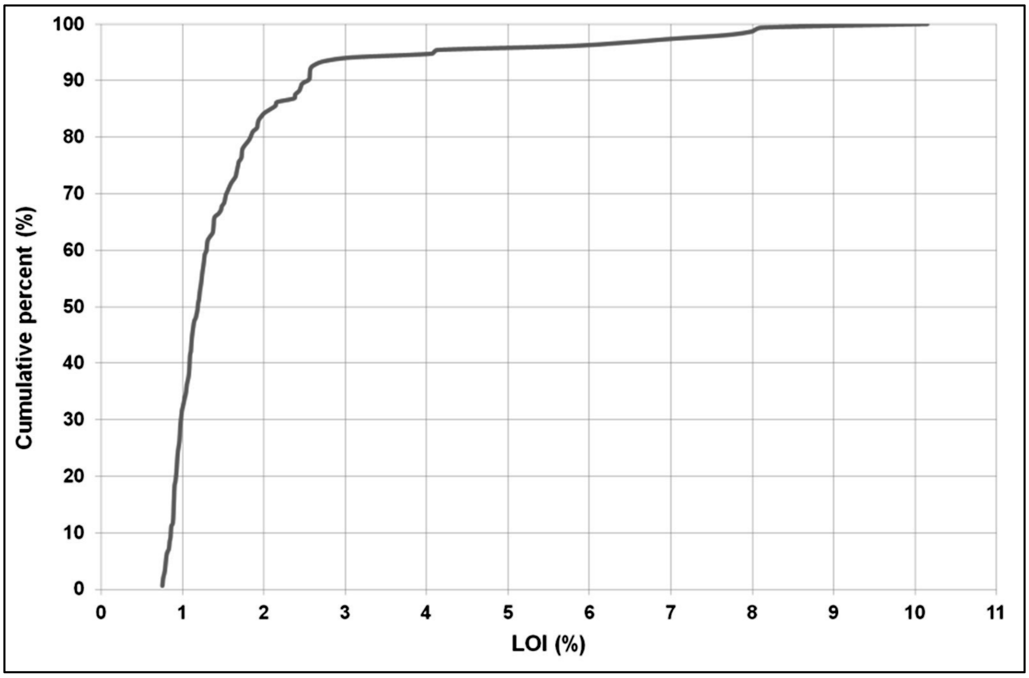


Figure 78 : Cumulative percentage of LOI values (measured on 152 hand-piece samples)

7.1.1.3 Three dimensional model

Based on the MAG and LOI measurements and the co-ordinates of the samples, for each factor, a three dimensional model of the quarry was created. In fact, this model shows the distribution of the MAG and LOI values in the quarry, which indirectly reveals the quality distribution of the reservoir. This model is based on the gathered data, the experiments, as well as the geo-statistical evaluations carried out on them. Figures 79 and 80 show the planar view of this 3-D model for MAG and LOI factors. The colors used in the models are defined by legends.

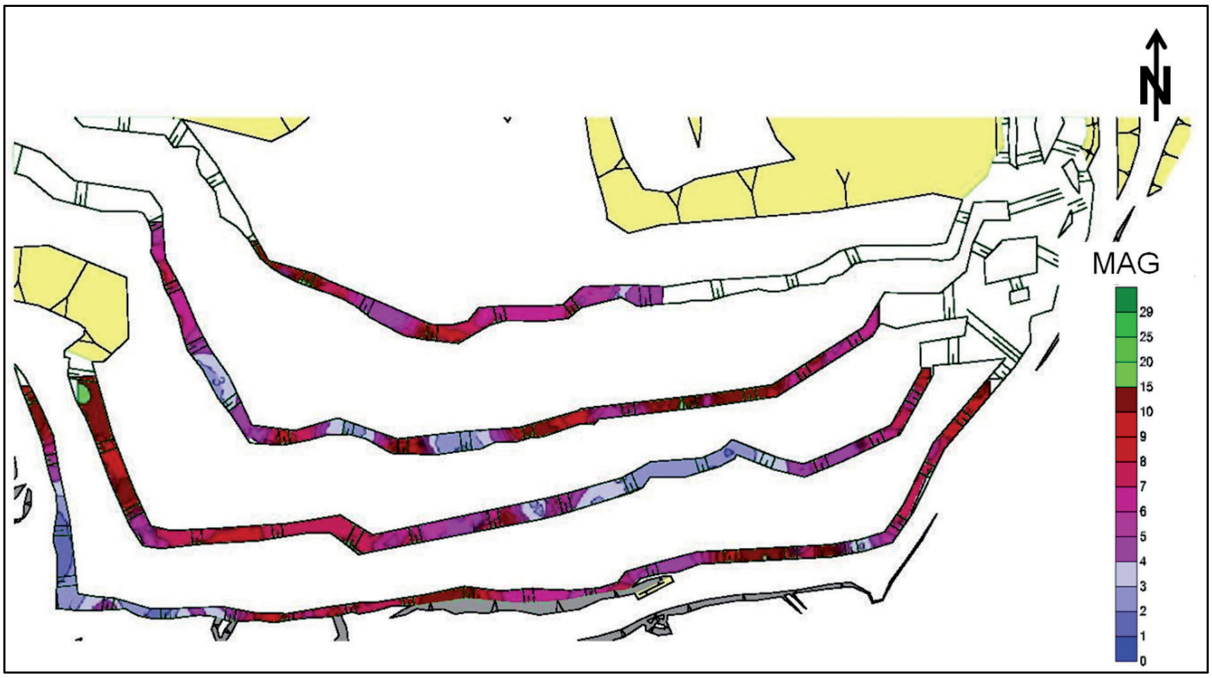


Figure 79 : Distribution of the magnetic susceptibility in the quarry

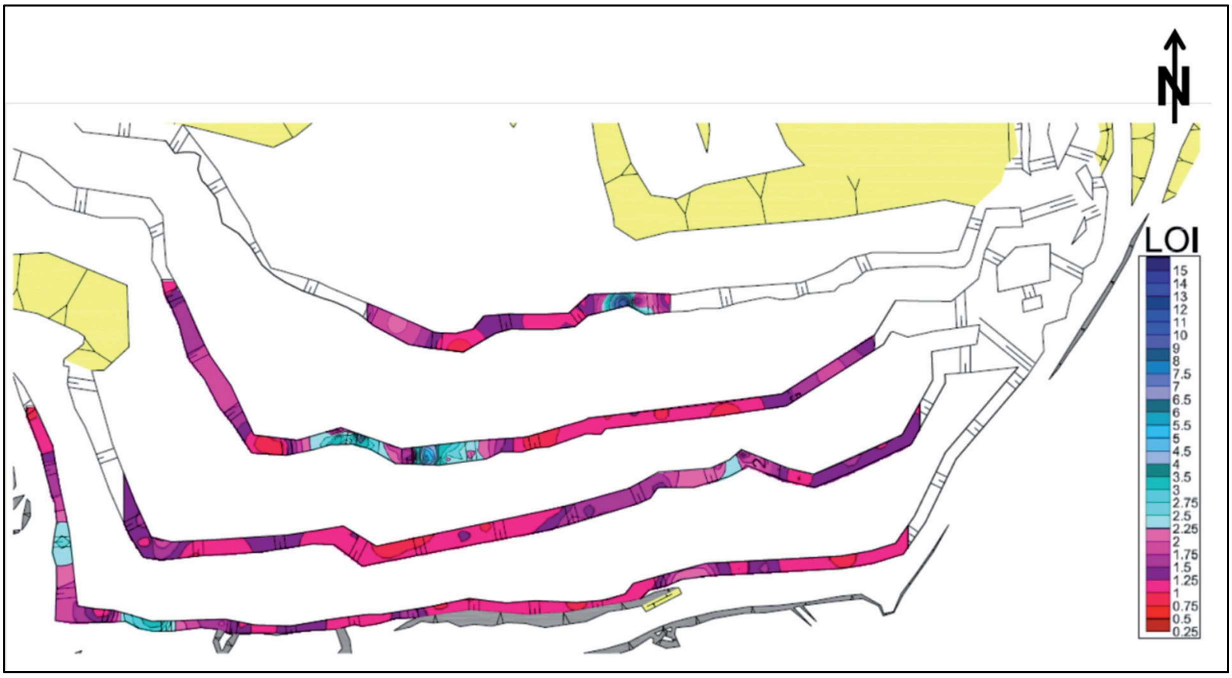


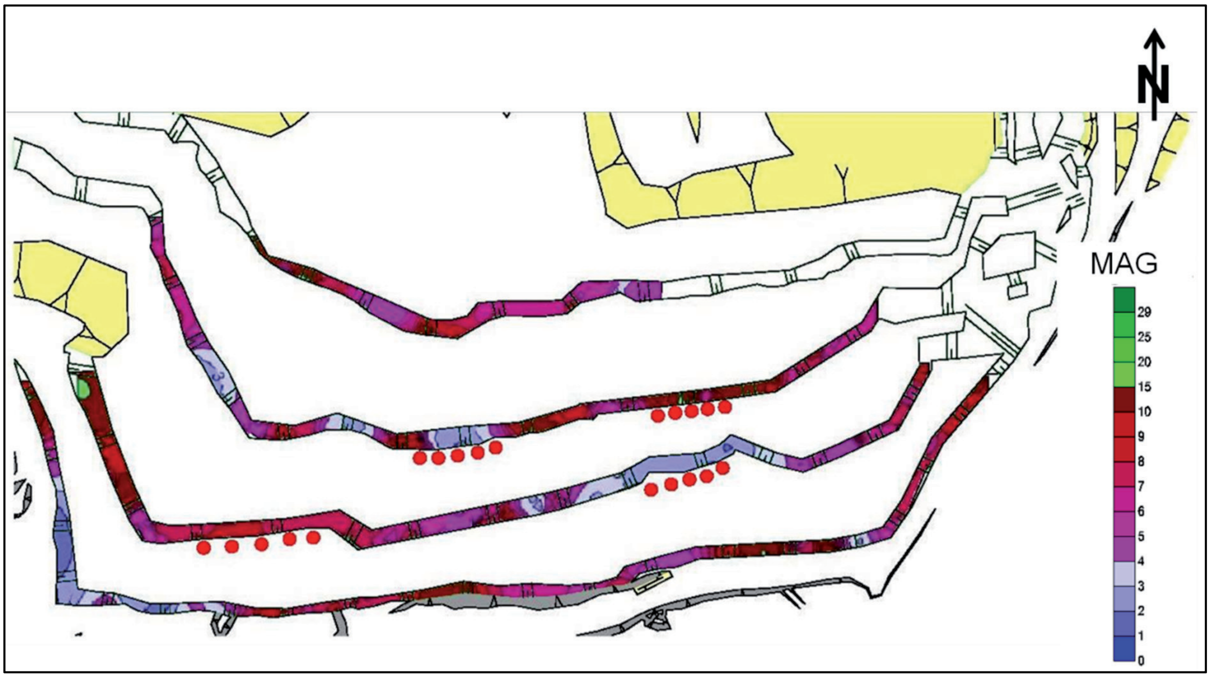
Figure 80 : Distribution of the loss on ignition in the quarry

7.1.1.4 Reproducibility control by means of drill holes

To control the reproducibility of the results obtained from the field tests, drilling of new boreholes were suggested. A total number of 20 drill holes (four groups of drill holes) were drilled on the benches. The location of drill holes were so designed that two regions with low quality rocks and two regions with high quality materials were covered (figure 81). The basis for quality recognition was LOI and MAG values of the drilling fines. LOI greater than 2% and MAG less than $3{,}00 \times 10^{-3}$ SI Units, implies to low quality materials and vice-versa. Figure 81 presents the location of the drilling boreholes.
The drill holes were between 20 and 22,5 meters deep. From every 5 meters interval, a representative sample was taken from the drilling fines (drill cuttings). At the end of the drilling process of each borehole, a representative sample was gathered from the whole drill cuttings. Five distinct samples were collected from each borehole (with each 20 meters deep): four samples from each 5 meters of the borehole and one sample from the complete drill hole. In this phase a minimum total number of 100 samples were gathered for further analysis in the laboratory. The samples were sent to laboratory and tested for their LOI and MAG values. At first, the samples were de-moisturized (dried in oven for about 24 hours with 100°C to 105°C, thus the surface

moisture was away). Then they were sieved with a 1mm sieve, afterwards the LOI and MAG experiments were applied on under 1mm size fractions. For MAG measurements, the same standard as defined before (using a plastic bucket) was applied. For LOI tests, about 5 grams of powder was weighed and put in a crucible and heated up to 850°C for two hours. As a result, a uniform standard method was always applied for the measurements and therefore the laboratory errors regarding the sample preparations were minimized.

Apart from loss on ignition and magnetic susceptibility experiments, a reference test was also applied on the samples to check the results of MAG, LOI and the detection limit. As reference test, the methylene blue dye test was performed by the company. The results of the methylene blue test also confirmed the MAG and LOI values as well as the defined limit of detection.



(a)

(b)

Figure 81 : Reference drilling holes shown on (a) MAG and, (b) LOI 3-D model

The drill cuttings from the boreholes were analyzed and did completely confirm the field measurements. Figure 82 shows the results on a 3-D model of the quarry (view from top). Having a quick view of figure 79, manifests the fact that the results of the field measurements do comply with the results of the drilling fines.

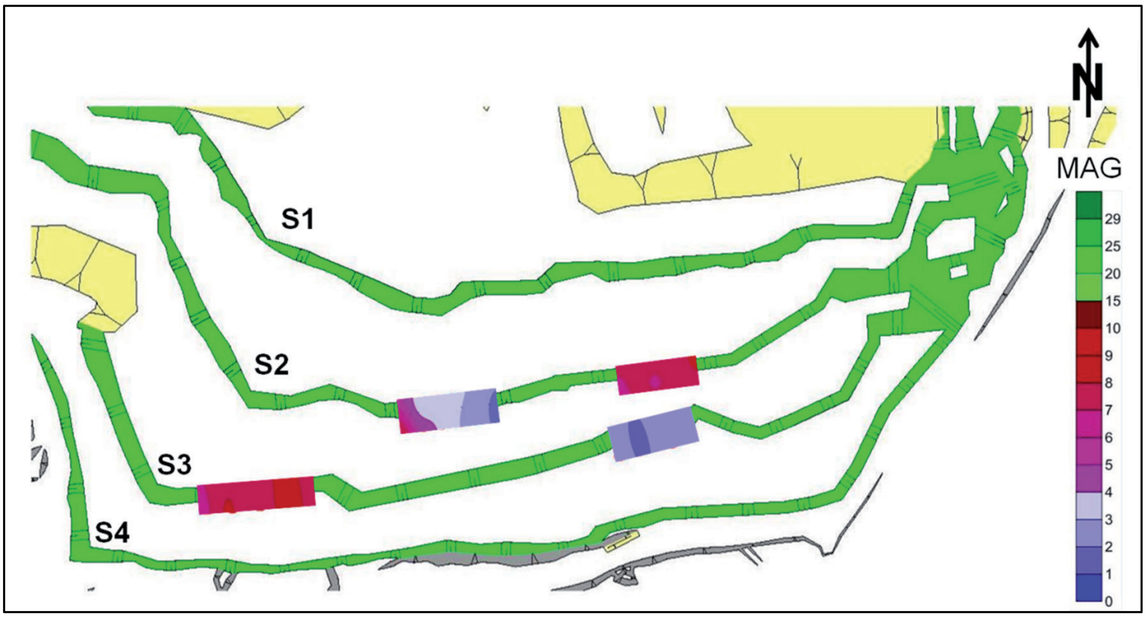


Figure 82 : Results of the MAG value measurements of the drilling fines (field experiments)

What could be concluded from this part of experiments is that the two defined quality factors (LOI and MAG) are firstly reproducible, secondly the defined counter-relation between them holds true here as well and last but not the least, they are both transferable on the drilling fines, which means they have the potential to be performed in the field and during drilling operations.

7.2 Laboratory experiments

Concurrent with the field experiments another 210 powder samples (from the old and new blasting boreholes) were collected and analyzed for their MAG and LOI values (the cuttings of the old blasting boreholes were previously gathered as reference samples for the laboratory). The drilling fines were prepared as before: dried, sieved by a 1mm sieve and then the LOI and MAG values of the fraction smaller than 1mm were measured. Figure 83 shows the results of the LOI and MAG values of the 210 samples. As it can be clearly seen, the inverse correlation between the LOI and MAG value exists here as well. Thus, this is another evidence that these two parameters are applicable for the early recognition of the quality of products.

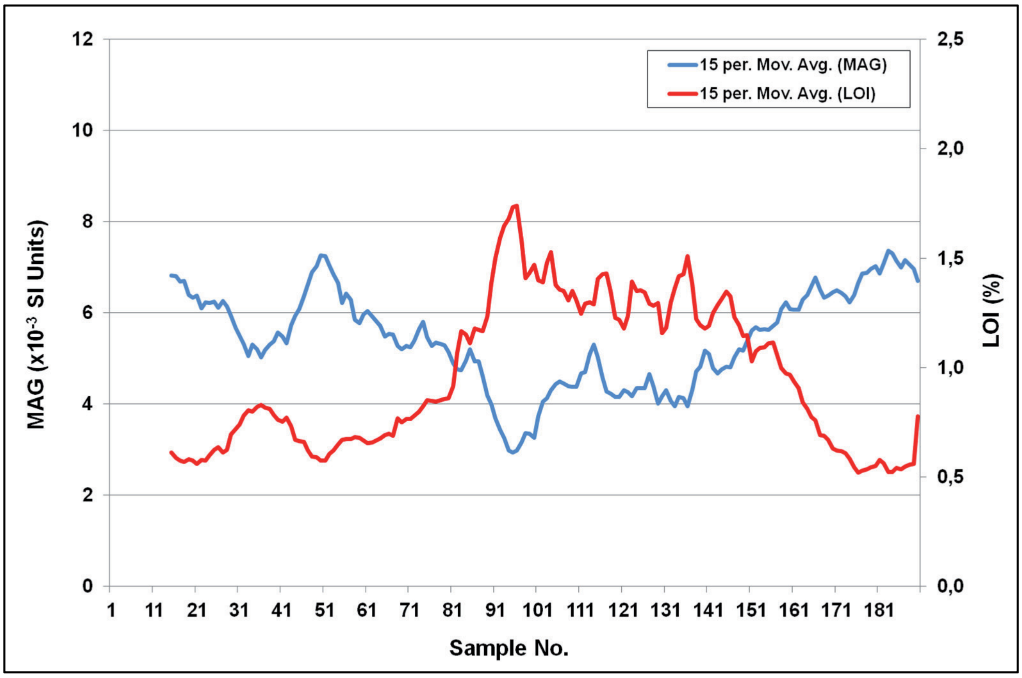


Figure 83 : MAG and LOI values of boreholes fines (210 samples)

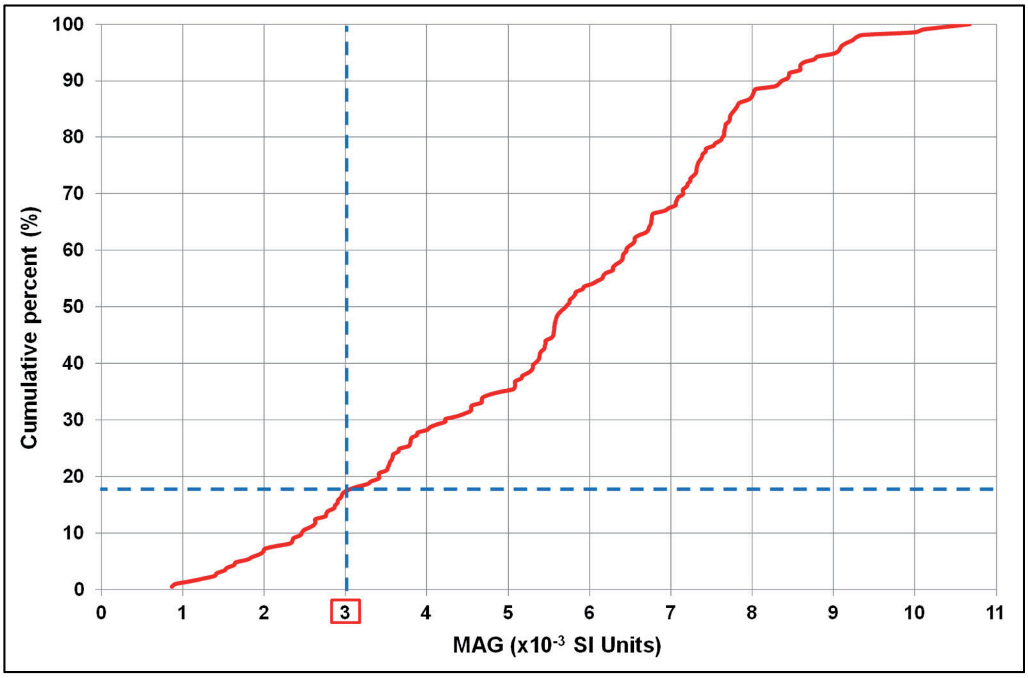


Figure 84 : Cumulative percentage of MAG values (210 borehole fines)

The same as earlier, with regard to a MAG value of 3,00x10^{-3} SI Units, about 20% of the quarry will have a low quality material and about 80% of it is remarked as high quality.

7.3 Results and discussions

The conventional methods used until now by the company were mainly glycol test and methylene blue dye test. As completely explained before, these methods are time consuming, not reproducible, not representative, not economical, and only applicable on hand piece samples from the quarry. They also do not correlate with each other, one piece of rock may be recognized as good quality with one method and as poor quality by the other method. Sometimes they confirm each other and sometimes deny each other. Therefore, there is no perfect fit between them. On the other hand, the two new developed criteria are quick, reliable, economical, and reproducible. As mentioned also before, between these two factors, the magnetic susceptibility has obvious advantages that makes it the first choice for quality assurance options. As it was confirmed in the detailed studies, this method has the ability to be performed directly on the borehole fines with the use of a portable device. It brings a lot of savings in time and of course time is money. This method has the potential to be applied directly in the field, during the drilling operation of the blasting holes and earlier than the blasting process. It means, before the materials are blasted there is the possibility to have information about the quality of the materials, whereas using the old methods (glycol and methylene blue) the company had to wait for the blasting operation. After blasting, a couple of hand-piece samples were gathered from the muck pile and sent to the laboratory for further experiments. Taking a couple of samples is never representative for the whole blasting muck pile. This is especially important when the quality variation in the quarry is extremely high. As explained in the third chapter, the range of hydrothermal alteration may vary from mm to km and in this case, this means that the quality may vary from one borehole to another (the spacing between blasting boreholes are normally 4 to 5 meters in the quarry). Thus, gathering only some hand-piece samples is not representative for the whole muck pile. On the other hand, on the day of drilling no sampling may be done, therefore the quarry has to wait for the blasting. On the blasting day, the samples are gathered (at the quickest) and sent to the laboratory. In earliest case, the day after blasting the preparation of the samples will start, and that is breaking the samples to smaller pieces and then drying for 24 hours under 100-105°C for glycol test or in case of methylene blue, drying, crushing, milling and then sieving (with 125 µm sieve). This means a time loss of at least two days after the blasting operation. Therefore, after the blasting is performed, the quarry has to wait at least two days in order to receive information on the quality assurance of the materials. This means the quarry shall not start with sending the muck pile materials to mineral processing plant, because the quality of the materials is not recognized yet. However, in reality, this is not possible. The quarry needs production and the customers need their requested and ordered materials. Thus what happens in the reality is that to avoid this loss in time, normally before the blasting, the wall of the working bench (where blasting is going to take place) is analyzed simply by eyes (visual observation mainly based on superficial color of the rocks and the experience of the person). The visual determination of the quality is done either by a geologist or by head of the quarry. Further visual sorting of the muck pile is also applied by the excavator´s operator while loading the trucks. Nevertheless, this may not always work. It shall be mentioned that a study on the colors of different materials was also carried out, but no distinct or specific rule was found. Therefore, trusting the color of the surface of the rocks is not sufficient to categorize the rocks from quality point of view.

Loss on ignition and MAG both have the possibility to be transferred on the drilling fines. However, since for evaluation of the LOI value a muffle often is needed and the materials have to be de-moisturized as well, LOI measurement will also take one day. Nevertheless, the MAG value is evaluated by a hand-held device and may be measured directly on the borehole fines, and there is no need for the materials to be sent to laboratory. It means MAG measurements and its corresponding results are presented in real time and this is the main advantage of MAG to LOI approach. Please note that, although for LOI results there is one day of delay, but this one day starts from the drilling date, which means at the blasting day and even before the blasting operation, the results are out and the mine manager knows whether the materials have high or low quality. Therefore, she/he is able to decide if all the boreholes shall be blasted in one time or not. Based on the old methods, the two days of delay starts after the blasting process which brings a great deal of uncertainty to the quality of the existing muck pile. As LOI and MAG have an inverse relationship, it is possible to select one of them as the quality control factor. However, in order to be certain and 100% confident about the quality, our suggestion is to measure both indices. As a matter of fact, although they correlate to each other in a wide range of situations, the correlation is not 100%. Actually, two distinct methods never correlate 100% with each other.

The study of the transferability of these methods on the drill cuttings of each borehole is of a great interest. As a result, the mine manager may analyze the quality of each individual borehole separately, and decide whether she/he shall blast all the boreholes at the same time. The situation may be so that in order to minimize the dilution effect, the quarry manager has to divide the blasting process into two stages, where in the first stage the poor quality materials are blasted, and in the second stage, the high quality materials are blasted. This is a strong tool that is presented to the quarry managers. On the other hand, if there is a little bit of uncertainty about the quality of the rocks from MAG values point of view, she/he has enough time to perform the LOI experiments as well and then decide about the quality with the highest level of confidence.

Based on the laboratory and field experiments performed till this phase, the limit of detection for LOI was set to be 2% and for MAG was $3{,}00 \times 10^{-3}$ SI Units. According to more than 8000 single measurements of magnetic susceptibility and in order to increase the degree of confidence, the MAG limit value was decided to be $4{,}00 \times 10^{-3}$ SI Units which leads to a LOI threshold value of less than 2%. This option will bring more certainty and accuracy for the quarry manager and corresponding authorities. In this case, about 30% of the quarry is regarded as low quality materials (figure 84).

Based on the explanations here and in the feasibility studies, the magnetic susceptibility is regarded as the first option for quality management purposes, whereas the loss on ignition may also be applied as an auxiliary factor, in case of uncertainties or in some special cases. In order to transfer the value of $4{,}00 \times 10^{-3}$ SI Units (which is a MAG value for drilling fines fraction under 1mm) directly over the drill cuttings at the operation site, further experiments must be carried out. As it is known, the drilling fines from the boreholes are a mixture of particles and not necessarily smaller than 1mm, this means the drilling fines do contain bigger size fractions up to 2 or 3 mm grains. Therefore, in order to be able to make the measurements directly in the mining site and on the boreholes, the laboratory MAG limit value of $4{,}00 \times 10^{-3}$ SI Units which is for materials under 1mm-sized grains, has to be correlated to the drilling fines coming out directly from the borehole. This stage is discussed in the next chapter where a vast number of field and laboratory measurements are highlighted. Correlation of laboratory values with field values would be the most important part of this phase of the study.

8 Field studies

The major goal in this phase is to correlate the limit of detection of MAG value gained in the laboratory (which is for drilling fines below 1mm fraction) to the MAG value measured directly on the drilling fines in the mining site. In other words the aim is to correlate the MAG limit of $4{,}00 \times 10^{-3}$ SI Units which is for fines under 1mm size to the corresponding MAG value of drilling fines from the bore holes and define a MAG threshold value for the drill cuttings. Based on our previous studies, the MAG values of drilling fines from the operating site shall be a little bit higher with respect to the laboratory MAG values. To determine this value a broad drilling and sampling program was scheduled.

8.1 Sampling of drill cuttings

A six months continuous sampling of borehole fines was planned in order to correlate and scale up the laboratory detection limit (of MAG) to field measurements. More than 300 boreholes were drilled in 6 months and a representative sample from each of the borehole fines was collected. As will be mentioned later on, the MAG values of the representative samples were measured directly at the site (at least ten distinct MAG measurements were done and then the average value was calculated and taken as the MAG value of the desired sample). Then the samples were sent to laboratory for further experiments. In the laboratory the samples were sieved with 1 mm sieve and the MAG values of under 1mm fractions were measured. Again, at least 10 single MAG measurements were applied on each sample and then the average value was taken as the sample MAG value. As a result of this phase of study, more than 6000 distinct MAG measurements were carried out on the collected samples.

The KT-10 hand-held device was used for the MAG measurements and the samples were collected in the predefined standard plastic bucket. MAG measurement were carried out within a standard format as described below.

In order to accomplish the measurements of this phase a special practical course was held for the laboratory and quarry staff to learn how to perform a correct sampling method, correspondingly collect a representative sample and then carry out the MAG and LOI measurements. For the sake of MAG measurements, a standard form was also designed and provided for the quarry and laboratory staff. Figures 85 and 86 show the layout of the designed standard form.

Messung der magnetischen Suszeptibilität					
Werk					
Sprengdaten			Labordaten		
Nr. des Haufwerks (Sprengung)			Auftragsnummer		
Datum der Bohrung			Probeneingang am:		
Nr. des Bohrlochs (Probenummer)					
Koordinaten der Bohrung (GPS)			Einzelmessergebnisse im Labor		
X			Datum der Messung		
Y			Name durchführ. Person		
Sohle			Unterschrift		
Einzelmessergebnisse am Bohrgerät			Einzelmessergebnisse Labor		
Datum der Probenahme			Einwaage M.in g	trocken M. in g	Wasserg. M.- %
Name der durchführenden Person					
Unterschrift					
1			1		
2			2		
3			3		
4			4		
5			5		
6			6		
7			7		
8			8		
9			9		
10			10		
Mittelwert			Mittelwert		
Bemerkungen					
Datum/Unterschrift Laborleiter					

Figure 85 : Standard form for magnetic susceptibility measurements in field and in laboratory (empty form)

Messung der magnetischen Suszeptibilität					
Werk					
Sprengdaten			Labordaten		
Nr. des Haufwerks (Sprengung)		26/10	Auftragsnummer	865-10	
Datum der Bohrung		25.08.2010	Probeneingang am:	26.08.2010	
Nr. des Bohrlochs (Probenummer)		4b			
Koordinaten der Bohrung (GPS)			Einzelmessergebnisse im Labor		
X	3425022.283		Datum der Messung	30.08.2010	
Y	5504195.622		Name durchführ. Person		
Sohle	4		Unterschrift		
Einzelmessergebnisse am Bohrgerät			Einzelmessergebnisse Labor		
Datum der Probenahme	25.08.2010		Einwaage M.in g	trocken M. in g	Wasserg. M.- %
Name der durchführenden Person			2310	2289	0,92
Unterschrift					

1		9,299		1		7,371	
2		8,597		2		7,206	
3		9,590		3		7,640	
4		10,350		4		7,544	
5		9,757		5		9,082	
6		9,431		6		7,572	
7		8,248		7		7,657	
8		9,829		8		8,154	
9		10,160		9		8,043	
10		9,055		10		8,396	
Mittelwert		9,432		Mittelwert		7,867	

Bemerkungen		
Datum/Unterschrift Laborleiter Rev. 2, 27.05.2010		Freigabe Dr.

Figure 86 : Standard form for magnetic susceptibility measurements in field and in laboratory (filled out by lab and field staff)

According to the trainings and provided standard form, the MAG values of all the 300 borehole samples were measured (in the field as well as in the laboratory). The trend of laboratory and field measurements curves is illustrated in figure 87. As forecasted, the laboratory measurements are a little below the field measurements. This is due to this fact that in drill cutting samples, the void spaces between the bigger grain sizes are filled out with smaller particles, thus making the samples denser and therefore causes higher magnetic susceptibility values.

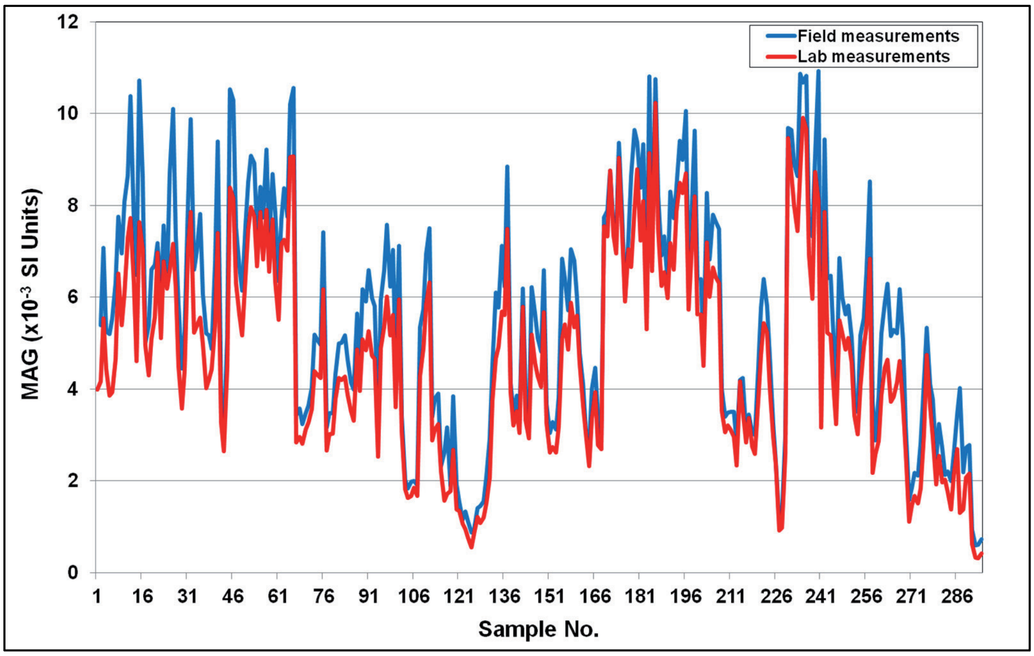


Figure 87 : Arithmetic mean (of the magnetic susceptibility) of field measurements vs. laboratory measurements

In figure 88, the measured values in field and laboratory are plotted against each other and as can be seen, there is a perfect correlation between them. If linear fit is applied to the graph, the regression coefficient is 0,9614 (R^2=0,9614) and if exponential function is applied then even a higher regression value of 0,9669 is gained (R^2=0,9669).

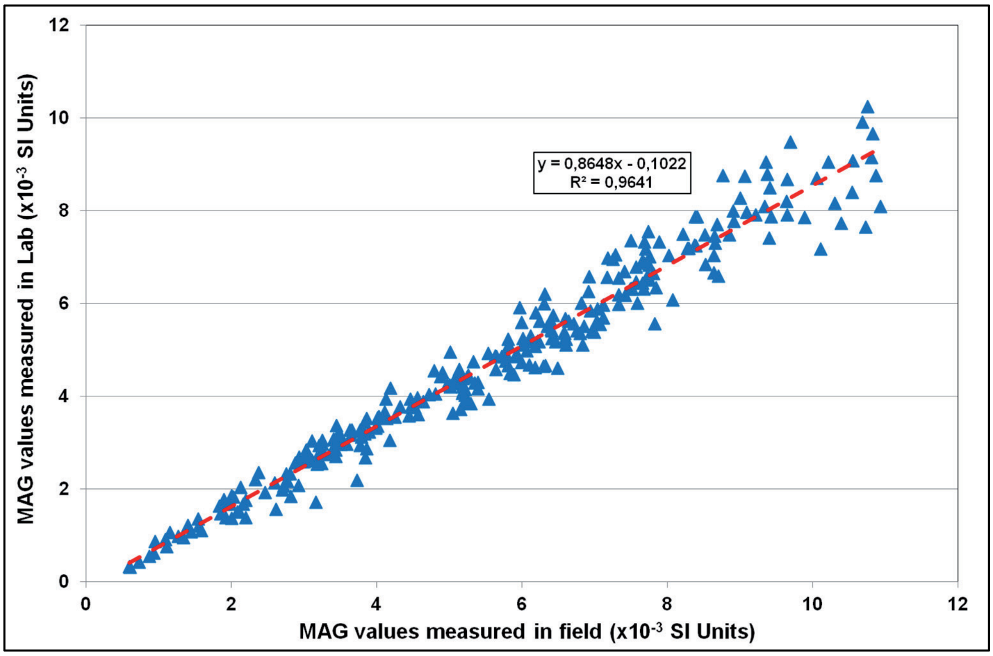


Figure 88 : Relationship between field and laboratory MAG measurements (linear fitting)

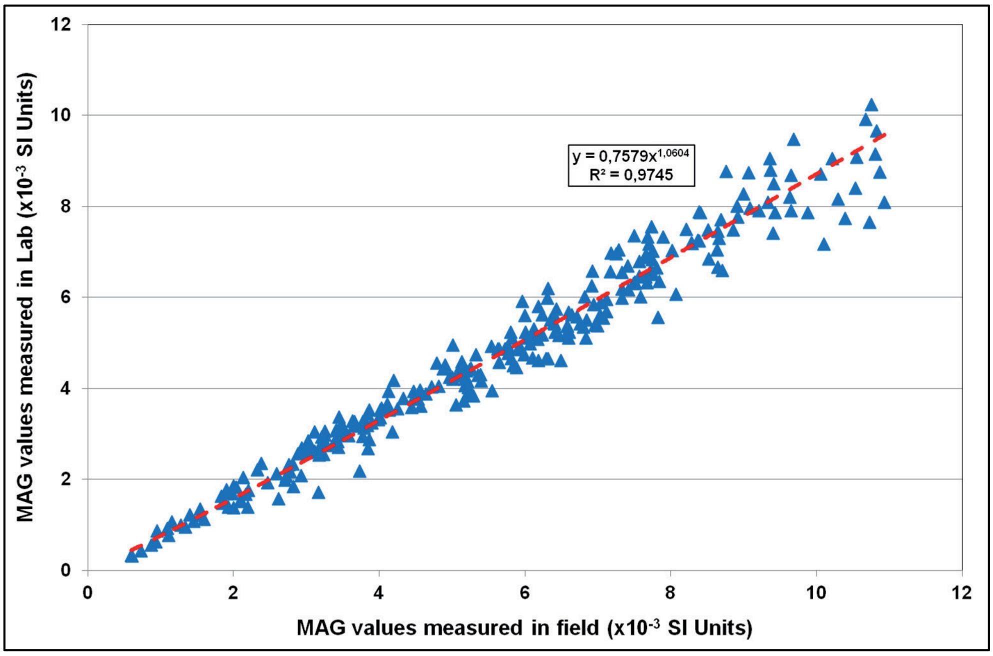


Figure 89 : Relationship between field and laboratory MAG measurements (exponential fitting)

8.2 Determination of MAG limit value for field measurements

In order to correlate the limit of detection (of MAG value) from laboratory to field measurements, two methods can be used. The first way is using the correlation graph between the MAG values measured in the laboratory and at the mining field (as in figures 88 and 89). Applying either of the correlation formulas obtained from figures 88 or 89, will return a value of 4,70x10^{-3} SI Units. The calculations are as below:

$$MAG_{Laboratory} = (0{,}8648 \text{ x } MAG_{Field}) – 0{,}1022$$

Or,

$$MAG_{Laboratory} = 0{,}7579 \text{ x } (MAG_{Field})^{1{,}0604}$$

Assuming the laboratory MAG value of 4,00x10^{-3} SI Units (as the threshold value for magnetic susceptibility), hence the limit of field MAG value will be about 4,70x10^{-3} SI Units.

The second way is applying the normalized difference method between the two measured data sets. In this case, the percentage of measurement variation with respect to laboratory measurements, is calculated for each sample. In other words, the difference between the (measured) MAG values in the field and in the laboratory for each sample is normalized with respect to the laboratory (measured) MAG values and is expressed as a percentage. This method of calculation is more accurate than the former method. For this reason, the method of normalizing with regard to laboratory measurements will be selected as the main approach to determine the limit of detection of MAG value for field operations. The normalized variation for each of the 300 drilling fine samples is calculated and then graphed. Figure 90 represents this method in a graphical way. The average value of the normalized variations is about 18%, which means the variation between laboratory and field measurements has a mean value of 18%. Based on this method, the relationship between the MAG values in laboratory and field will be:

$$M_F = M_L \cdot \frac{18}{100} + M_L$$

Where;

M_F = MAG values measured in the field
ML = MAG values measured in the laboratory

According to the above formula, fixing the MAG value for laboratory measurements as $4{,}00 \times 10^{-3}$ SI Units, the MAG value for filed measurements will be $4{,}72 \times 10^{-3}$ SI Units. This value also confirms the value calculated from the first method (from the correlation formulas).

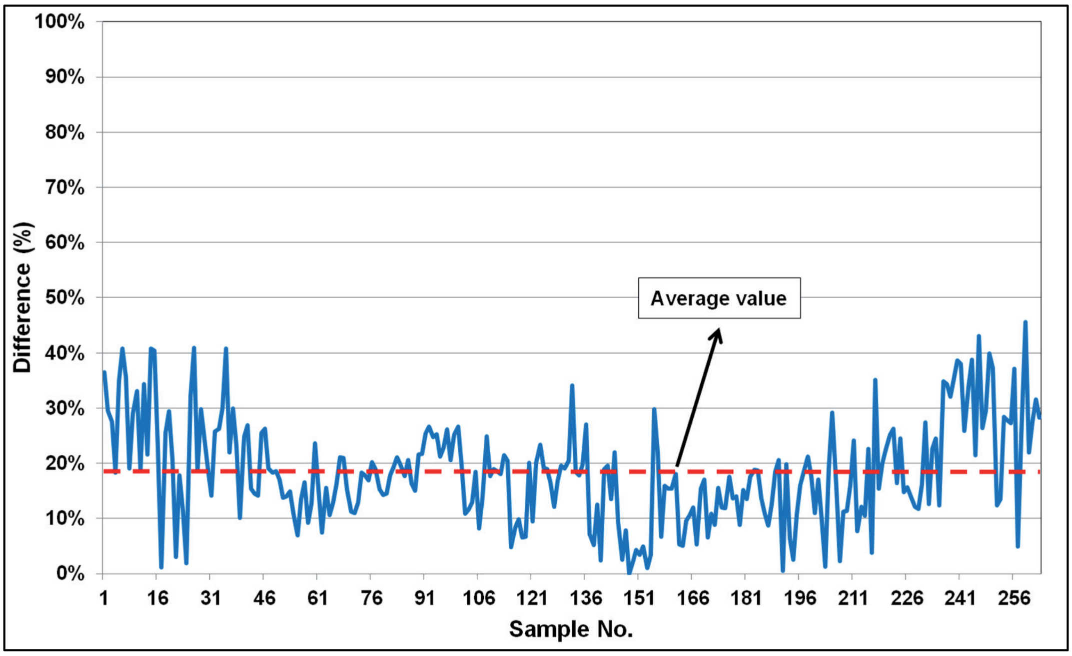


Figure 90 : Variation of normalized differences of the drilling fine samples

The calculated MAG threshold value for field measurement will be controlled from the statistical point of view as well. Figure 91 shows the scatter graph of MAG values gained from laboratory and field measurements. The data is obtained at least from 300 MAG value measurements (from borehole drill cuttings). Based on the MAG limits for laboratory ($4{,}0 \times 10^{-3}$ SI units) as well as for the field ($4{,}70 \times 10^{-3}$ SI units), the graph is divided into four quadrants namely I, II, III and IV.

Quadrant I shows the region where according to the laboratory measurements the sample is categorized as good quality but according to field measurements is low quality samples. Quadrant II is known as good quality samples for both measurements. Quadrant III is for low quality materials with respect to both measurements and quadrant IV is recognized as low quality materials for laboratory while regarded as high quality with respect to field measurements.

Based on the above description the measurements in quadrant II and III, have the correct correlation between the field and laboratory measured values.

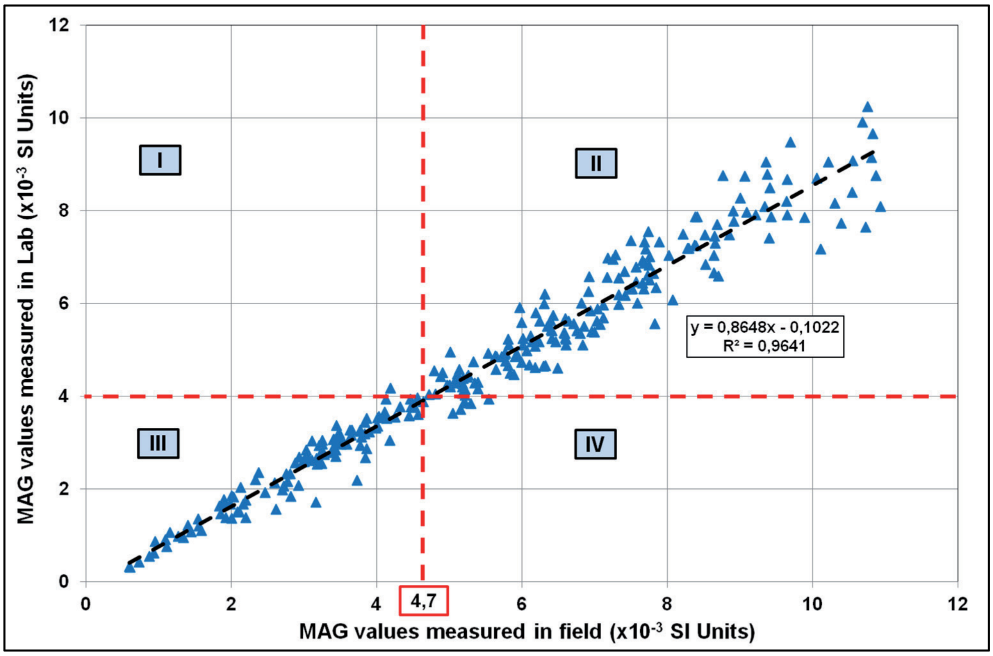


Figure 91 : Statistical controlling of the field MAG limit value

A short discussion is necessary regarding figure 91. As mentioned, the samples in quadrants II and III have the right correlations and are either known as good quality materials or poor quality materials by both measurements. The main debate arises when samples are laid in quadrant I and IV. As clear in graph 91, only one sample lies in quadrant I. This means, it is a good quality sample in the laboratory but poor quality sample in the field or production site. Only one sample out of about 300 samples counts around 0,3% of the whole samples which is negligible. On the other hand, seven samples lie in the 4th quadrant, which counts about 2% of the whole samples. These seven samples are recognized as good quality materials in the field but poor quality materials in the laboratory. Further analysis about why these samples are lying in quadrant IV revealed that these samples had a MAG value of slightly lower than 4,00x10^{-3} SI Units in the laboratory (also viewable in figure 91). Based on the accuracy of the measurements, this small variation from the laboratory MAG limit value may be rejected.

Therefore, according to the measurements and discussions, the MAG limit value (of drill cuttings) for operation fields/sites will be 4,70x10^{-3} SI Units.

8.3 Determination of MAG limit value based on fractal analysis - A quality control approach

To confirm the defined limit of magnetic susceptibility value for quality control (QC) purposes, the “fractal analysis” method is adopted. Fractal analysis is a strong tool for statistical data evaluation and analysis. Fractal models have been applied to geo-sciences and mineral resources since the last four decades and they are used to define the geochemical thresholds in different anomalies. The geochemical data have normally fractal behavior and may not be studied by conventional statistical methods such as normal distribution or histogram analysis, instead it is deduced that these types of data have a fractal distribution models [188] [189] [190] [191] [192] [193]. In this section, it is manifested that our gathered data obey the fractal model.

8.3.1 Descriptive analysis

As the first step, a descriptive analysis was applied on the magnetic susceptibility data gathered from 204 drill cuttings. Figure 92 shows the MAG value frequencies.

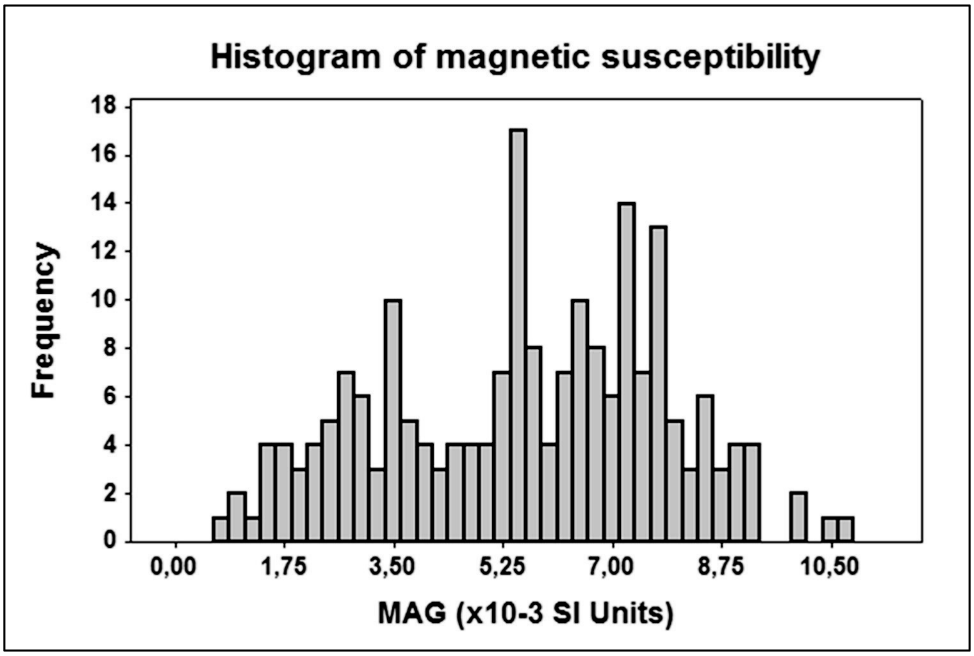


Figure 92 : Histogram of magnetic susceptibility (204 drill cutting samples)

At the first glance, the frequency of the magnetic susceptibility reveals the fact that the gathered data does not follow a normal distribution. Based on this information the assumption of the existence of more population groups in the gathered data was empowered. Thus, the concept of a bi-modal and tri-modal distribution (instead of uni-modal distribution) for the collected data set came to realization.

8.3.2 Probability graphs

To be able to predict the multimodality of the MAG data and then precisely define the number of different populations/groups in the collected MAG data from 204 samples, the probability graph of the data set was plotted. As shown below (in figure 93) the inflection point in the probability graph reveals the fractal characteristics of the data and shows that the MAG data has a bimodal distribution. The point of separation of the two different populations, lies exactly on the inflection point and is approximately $4{,}70 \times 10^{-3}$ SI Units. This value is exactly the MAG value that was defined as the limit of detection for quality control purposes in the former sections. Separating the population from this point (X=4,70) will give us two distinct populations. Each of these distinct populations (shown in green and blue in figure 93) have a normal distribution. In fact the bimodal distribution is separated into two unimodal ones.

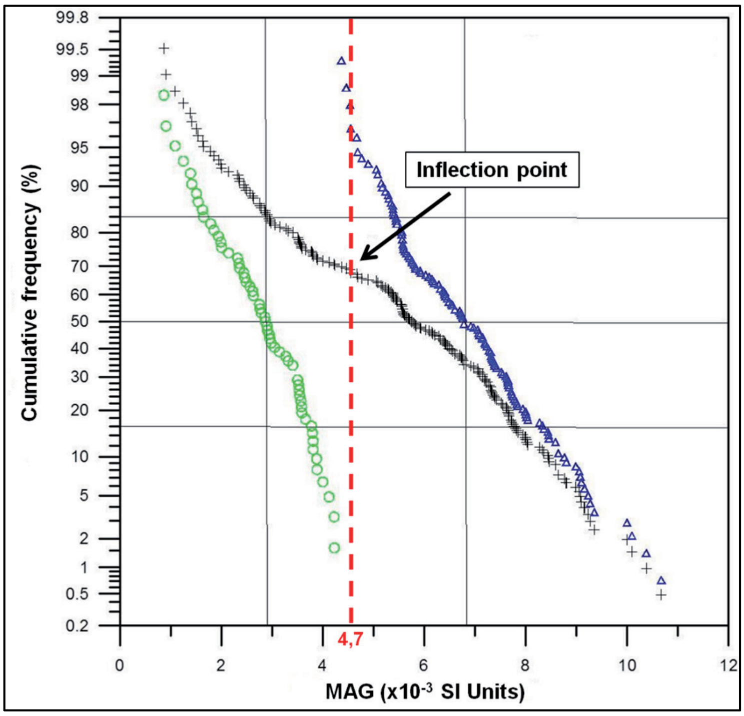
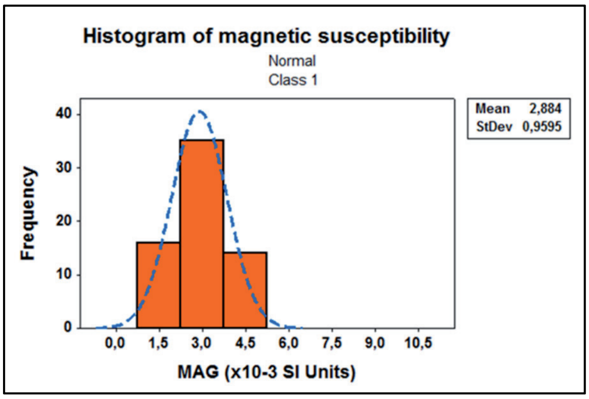


Figure 93 : Probability graph of magnetic susceptibility (data from 204 drill cuttings)

The fact that the green and blue curves have a linear trend in figure 93, confirms this idea that they both follow a normal distribution.

According to the inflection point (MAG value of 4,70x10^{-3} SI Units), the populations are separated and the histogram of each population is shown separately in figure 94. As it is clear, they both comply with a normal distribution. This issue confirms the fact that was discussed (regarding the probability graph) in the last page.



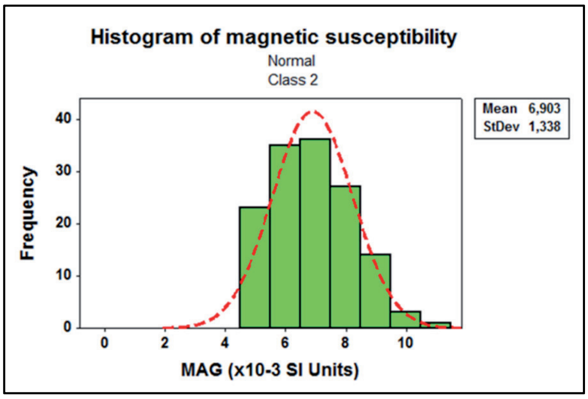


Figure 94 : The histogram of separated populations

A better schematic histogram of the whole data set is depicted in figure 95. It is very clear here that the two populations are separated from each other at approximately MAG value of 4,70x10^{-3} SI Units.

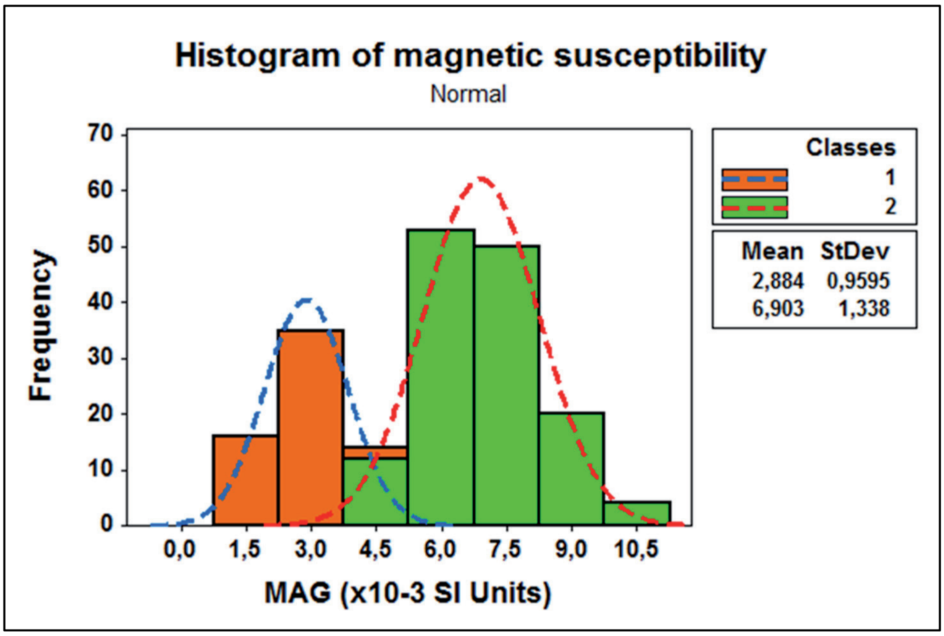


Figure 95 : Histogram of the whole data set presenting a fractal behavior of the collected data (bimodal distribution)

8.4 Results and discussions

A detailed field study was performed in order to approve the transferability potential of the two developed methods in to the operation sites and directly on the drill cuttings. It was confirmed that both methods could be applied on the drill cuttings. However, because of the advantages of magnetic susceptibility measurements, one of which is the time aspect, it was deduced to take the MAG index as the primary quality control factor and LOI as the secondary factor. It is important to note that in case of any doubts about the material quality, LOI evaluation can be performed simultaneously with MAG measurements.

The threshold of MAG value as a quality criterion was defined and confirmed not only via laboratory and field experiments but also via fractal analysis method. The MAG limit of detection was $4{,}7 \times 10^{-3}$ SI Units for the drilling fines. This means the drilling fines exposing a MAG value less than the defined threshold are categorized as poor quality material and higher than this value will be grouped as high quality. Since the samples of drill cuttings are good representations from the whole rock mass column underneath each drill collar (about 20 meters of height), the quality of the muck pile can be estimated with a high degree of confidence. The MAG measurements can be applied on the borehole cuttings at the time of drilling operation with a simple easy to take hand-held magnetic susceptibility device. In other words, the quality evaluations are performed in real time and online. At the end of the drilling time, the quality of the entire un-blasted rock mass (which will be blasted respectively) is perfectly recognized. This early recognition about the quality of the muck-pile/blasted rock helps the quarry manager to decide if the materials shall be sent for railway ballasts applications or not.

A special standard form was designed to be used by the authorized quarry staff engaged with MAG measurements. The (performed) measurements on the representative cuttings sample of each borehole, are written on a separate sheet of form and then entered in an excel sheet which is later analyzed by the mine manager. The MAG threshold value of $4{,}70 \times 10^{-3}$ SI Units has been applied (by authorized persons of the quarry) on the drilling fines since 2010 and until now no further compensations were claimed. It shall be mentioned that in case of any sharp change in the mineralogy and lithology of the quarry, we will be informed immediately and the threshold will be updated.

At the end of the studies, based on the MAG data gathered from the drilling fines, a three dimensional model of the quarry was developed. Figure 96 shows the 3D model of the quarry. The green colored locations have high quality materials whereas the red color depicts the poor quality materials.

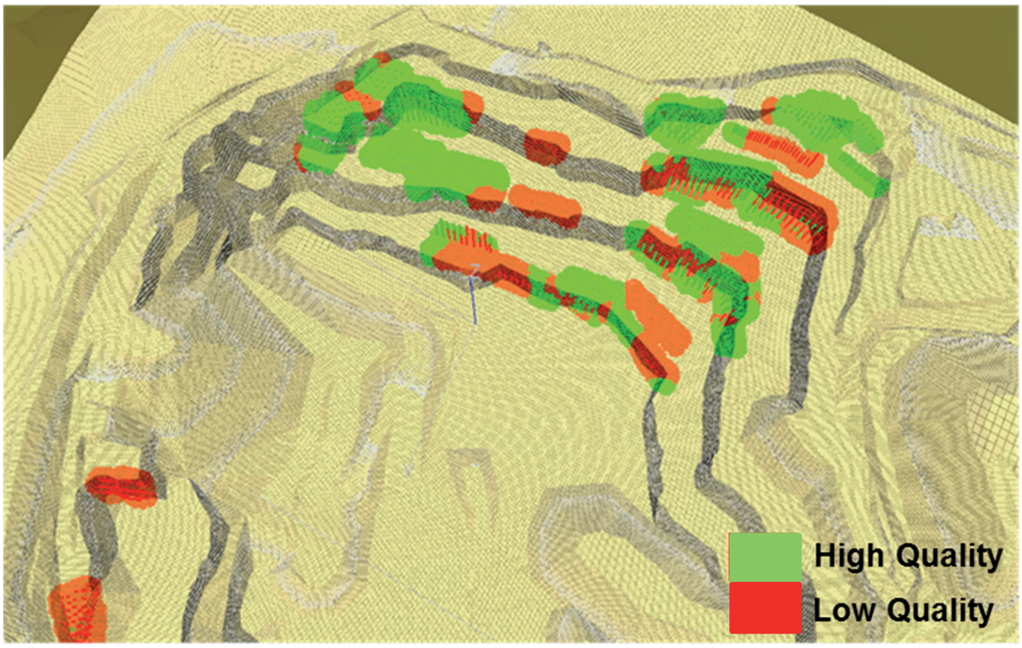


Figure 96 : Three-dimensional model of the quarry based on the magnetic susceptibility measurements of the borehole drill cuttings (green color=high quality materials, red color=poor quality materials)

9 Asphalt quality and aggregate water discharge theory

After the detailed laboratory and field studies on aggregate quality evaluation for the sake of railway ballast applications, two indices were developed: loss on ignition and magnetic susceptibility. As discussed before, the magnetic susceptibility was chosen as the first option and the transferability of its application from laboratory scale to field scale was proven. A threshold for this indicator was also presented which means materials having a magnetic susceptibility under this limit are grouped into low quality materials and above the limit are categorized into high quality materials. The limit of detection for recognizing low quality from high quality materials was defined to be $4,70x10^{-3}$ SI Units for the borehole drill cuttings.

In the next chapters with this knowledge, we will further discuss the impact of the defined indicators on the quality of asphalt. It would be interesting to find out whether or not these parameters have any particular effect on the asphalt quality.

As perfectly explained before, it is since decades that asphalt-producing companies confront major problems regarding the quality of their produced asphalt. One of these serious problems is the affinity failure, which is the loss of adhesion between the bitumen binder and aggregate surface. The corresponding asphalt production plant, which is the main concentration of this part of research project, also suffered from this problem and they sometimes got compensations because their produced asphalt quality did not meet the defined requirements of the authorities. The loss of adhesion between bitumen and aggregate surface which in the asphalt industry is known as "stripping" causes further significant problems namely loss of asphalt stability as well as asphalt swelling.

Full knowledge of material flow from a quarry to asphalt plant and finally to asphalt construction site is crucial for analyzing this problem. In fact, what happens in a typical Hot Mix Asphalt plant (HMA plant) is that the igneous hard rock, which is mined from the quarry, is crushed and classified in different grain sizes and then transported to asphalt plant. In an asphalt plant, different aggregate classes are weighed and mixed based on a special recipe for being heated in a dryer drum and then mixed with bitumen in a mixer. The final product or asphalt, which is a mixture of bitumen, aggregates, and some other additives, is then transported to the construction site. The problem is that in some cases a while after asphalting the roads, streets, or expressways, the asphalted roads start to strip (under natural conditions) and after a period of time, the asphalted surface is (partly or even completely) damaged. The asphalt plant under consideration of this research work also encountered the same problem. The primary evaluations carried out by the company showed that the asphalt of the damaged sections suffered from a low stability and high swelling factors.

In chapter three of this research work, detailed description of problems confronting the asphalt industry and their possible related solutions were presented. Most of them discussed about the chemistry of bitumen and aggregates. The best solution presented regarding this problem was to use additives in order to increase the adhesion force between bitumen and aggregate surface. A debate on the application of instinctual characteristics of the aggregates themselves is rarely under focus. The qualities of aggregates do play an important role, which is not much discussed in the similar works. To solve adhesion problem by the use of the rock nature, a comprehensive basis concerning the characteristics of the rock is needed. Information regarding the rock itself such as type, nature, mineralogy, formation, constituents, physical and chemical properties could lead us to the right path. A better solution can be suggested only after gathering the right information regarding the nature of the rock.

For this study, since the aggregates from the same rock type (which were used as railway ballasts) were also consumed in the asphalt plant, therefore the preliminary information regarding the rock was already available. The rock aggregates are basalt-andesit type and based on the quality control evaluations, they may dispose different qualities. The main aim of this part of the study is to evaluate the transferability of the defined indicator(s) to asphalt industry and to determine whether these indicators would minimize the stripping effects and enhance the quality of the asphalted roads. On the other hand, based on the developed quality indices and with regard to the loss of adhesion problem, a new theory is presented. Afterwards the possible solutions to this long time problematic issue are also discussed.

To have a better understanding of the HMA production cycle, we will start with a brief description about this issue and then the new theory will be introduced.

9.1 Hot Mix Asphalt production cycle

After natural rock is mined from the quarry, it is sent to the processing plant, where it is crushed, sieved and then categorized into different grain size ranges such as 0-2 mm, 2-5 mm, 5-8 mm, 8-11 mm, 11-16 mm, 16-22 mm, 22-32 mm and 32-56 mm.

Then the natural crushed stone (or aggregates) is delivered to asphalt production plant where based on their grain sizes they are stocked in the pre-defined storage bunkers. Figure 97 shows a schematic view of an asphalt plant.

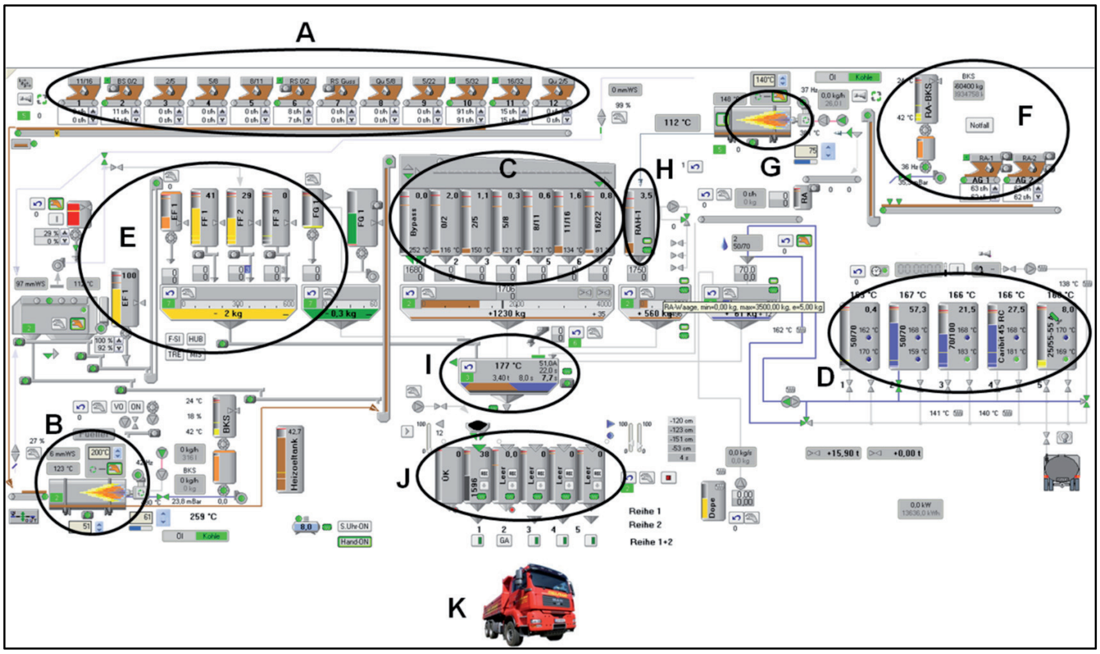


Figure 97 : Flow sheet of an asphalt production plant [194]

In order to have a better idea about the different sections of an asphalt plant, the major parts and their functionalities are described briefly below (different sections of a typical asphalt plant were displayed in figure 97).

Section A (aggregate bin feeders): The natural crushed rocks or aggregates are stored in a so called "aggregate feeders" or bunkers based on their grain sizes, e.g. 0-2 mm, 2-5 mm, 5-8 mm and so on.

Section B (aggregate dryer drum mixer): The aggregate bin feeders discharge the aggregates on a conveyor belt underneath them so that they are transported to the dryer drum mixer. The mixture of aggregates enters the dryer drum from one side and exits from the other side. The dryer drum is about 10-12 m long, has a diameter of 2-3 m and is installed at an angle of 3° to 6° for a better flow of material (smaller size dryer drums are also available). The materials inside a drum are heated with a burner flame. The new technology dryer drums are a counter flow drums, which means the hot gas stream produced by the burner flow in a counter current direction to the flow of aggregate material in the drum (figure 98). It takes a minimum of seven minutes for the materials to pass through the drum. The burner of the drum has a temperature of about 750°C. The main aim of the dryer drum is to reduce the moisture of the aggregates (to about 0,5% by weight).

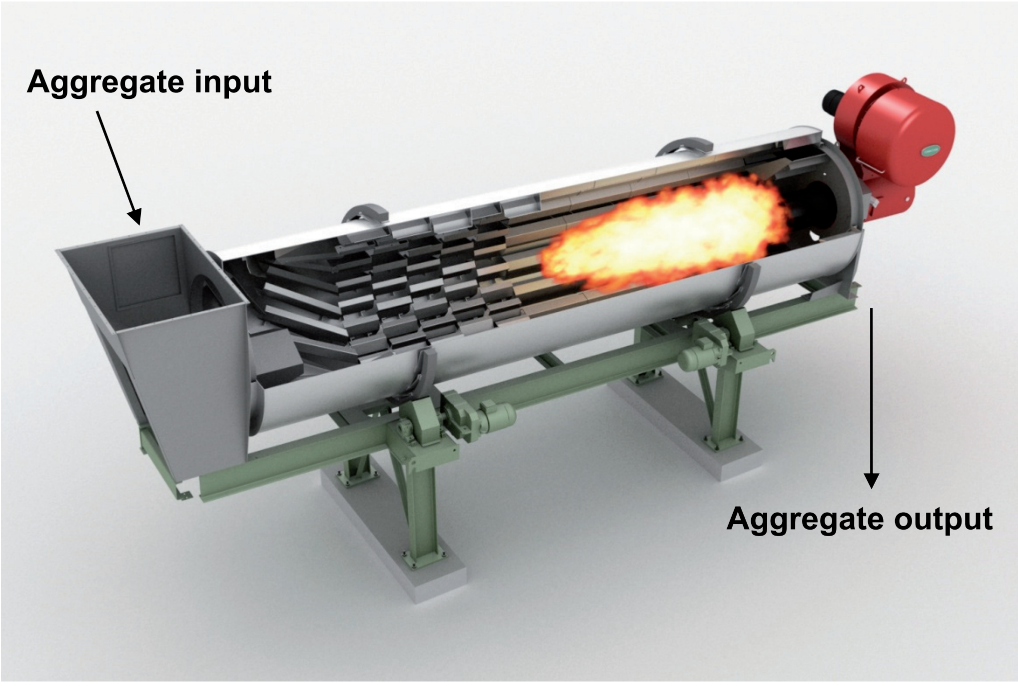


Figure 98 : Overall view of a counter flow dryer drum [194]

Section C (hot aggregate storage silos): After the aggregates are heated, the output of the dryer drum is sieved and the hot aggregates are categorized again into different grain size ranges. Afterwards they are stored in different silos on the basis of their grain sizes (e.g. a silo for hot 2-5 mm grain size, another silo for hot 5-8 mm size fraction and so on). The hot aggregates are then weighed and fed to the mixer (according to a predefined recipe). The storage phase duration may take from minutes to several hours.

Section D (bitumen storage silos): Different types of bitumen (e.g., 20/30, 50/70, 70/100) are stored in these silos. The temperature of the silos is about 160°C to 170°C. Bitumen is weighed based on an assigned recipe and then transported through special pipes to the mixer.

Section E (silos for mineral fillers/additives): The mineral fillers/additives are stored in these silos. The mineral fillers are divided into two groups: foreign/external fillers (e.g., lime stone powder) and own/internal fillers (powder and dust of the same rock aggregate being used to produce asphalt, it is mainly collected in the bag-house). The fillers are weighed and then added to other materials in the mixer.

Section F (bin feeders for recycled asphalt or RA): The recycled asphalt is stored in these bins. The conveyor belt beneath the feeder transports the materials to the recycled asphalt dryer drum.

Section G (recycled asphalt dryer drum): This dryer drum is used for the recycled asphalt. The recycled asphalt, which is in fact a finished asphalt product (aggregate and bitumen) is also heated up to a specific temperature in order to be prepared for further processes.

Section H (recycled asphalt silo): The heated recycled asphalt is stored in this silo. It is also referred as recycled aggregate silo.

Section I (mixer): Different components of asphalt such as aggregates, bitumen, additives or in special cases the recycled asphalt are weighed (in their hot forms) based on a particular recipe and then entered to the mixer. These constituents are mixed together in the mixer for some minutes in such a way that the output product is homogenous hot mix asphalt.

Section J (HMA storage silos): The HMA discharged from the mixer enters to the HMA storage silos. The HMA may be stored in these storage silos from a couple of minutes up to 24 hours. However, the storage duration shall be minimized as much as possible.

Section K (asphalt transport): The finished product of HMA is loaded into special road trucks and then transported directly to the construction site. The transport duration may take up to one hour.

9.2 Water discharge theory

As mentioned before, the main concentration of this part of our research work is on the affinity problem between aggregate surface and bitumen. When the adhesion bond between bitumen and aggregate is lost, the affinity between these two materials decreases and leads to a partly or complete stripping of bitumen layer from the aggregate surface. Water is known as the major player in this issue. Different mechanisms and theories regarding this problem were discussed before (in chapter 3).

In this research work, based on the detailed studies of the rock quality indices, a new theory regarding the affinity and adhesion problem (of asphalt) is presented. This theory, which is named as “water discharge theory” deals with the occurrence of adhesion loss in bitumen-aggregate system and discusses the probable reasons of this phenomenon.

According to this theory, every aggregate (as a single particle) contains water in different forms/phases, which tends to evaporate from the aggregate particle because of heating (or rise in temperature). A part of aggregate water shows itself as water vapor tending to get out the aggregate and at the same time exerting excessive pressure on the bitumen film around the aggregate surface. As a result of this action, craters and bubbles are created in/under the bitumen layer which serve either as an entry point or as an accumulation/assemblage space for water. The other portion of aggregate water could be trapped as water vapor underneath the bitumen film and condensate in the next phases (cool down phase of asphalt mixture) leading to the formation of a thin water layer between bitumen and aggregate surface. In either cases (getting out or being entrapped), the water vapor damages the bitumen layer. This results in loss of adhesion between bitumen and aggregate thus stripping of bitumen from aggregate surface.

Regarding the existence of different forms of water within the crystalline structure of a substance, it shall be noted that beside moisture, which is the simplest form of water found on the surface of an aggregate, crystal water, pore-water, capillary water, and gel water exist as well. Heating of rock aggregates or powders up to high temperatures (as in LOI) causes the volatile constituents to be eliminated. The volatile components are mainly water, carbon dioxide, carbonates, sulfur dioxide, and some clay minerals. Water and carbon dioxide, which are the major volatile components, will evaporate at 300°C-350°C. Carbonates start to break down and eliminate in temperatures higher than 450°C-500°C, and the clay minerals need even higher temperatures (up to 1100°C) for their elimination.

In case of HMA process cycle, aggregates are either heated in the aggregate dryer drum or in the RA dryer drum. The measured temperatures at the outlet of aggregate dryer drum showed a maximum surface temperature of about 320°C and in case of RA dryer drum it was about 130°C. It shall be mentioned that at a specific time, the inner temperature of aggregates is less than the surface temperature. Figure 99 shows how a particle starts to increase its temperature by means of convection heat transfer.

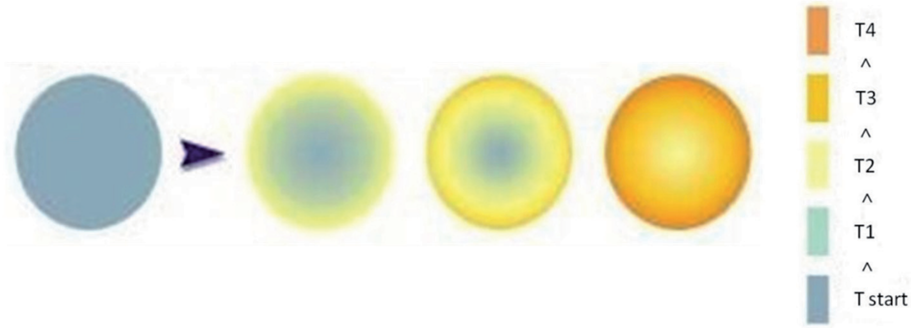


Figure 99 : Material heating and convection heat transfer [195]

Figure 99 presents this fact that when aggregates are inside the dryer drum, they absorb the heat of the burner flame by means of convection process. The heat transfer or warming process starts from the surface (of an aggregate), penetrating toward the center. Therefore, first the surface starts to warm up and then the heat is transferred toward the central parts. Thus, it takes time for the heating energy to reach the center of an aggregate. It means in a dryer drum where the burner flame has a temperature of about 750°C, based on the retention time of the aggregates inside the drum, which is about 6 to 7 minutes, the aggregate surface reaches a temperature of about 230°C and the core of the aggregate will have a lower temperature. Of course, the transferability of the heating energy is a function of time, aggregate constituents, mineralogy, and the size/radius of the aggregate.

According to our performed measurements, an aggregate particle coming out from the dryer drum has an average temperature of 230°C to 330°C. Up to these temperatures, water (in different forms) is the main component that is regarded as the volatile substance. Therefore, water starts to evaporate in form of vapor or gas.

In figure 100, the theory of “discharge water” is schematically presented. In phase 1, the aggregate is shown prior to heating, which means it contains moisture and other forms of water. In phase 2 it enters the dryer drum and starts to dry out but since the retention time in the dryer drum is not long enough, not all the water content of the aggregate particle is completely eliminated. In Phase 3, while the aggregate is hot and therefore is in water evaporating stage (out gassing phase), the bitumen is added to it (in the mixer) and the mixing process takes place. What happens after mixing process is that either water will be stored in form of water vapor at the interface area between aggregate surface and bitumen or it will damage the thin bitumen film while getting out as gas. In phase 4 since the aggregate is still hot, the residual volatile water tries to get out. This process will continue and the rupture of bitumen film and storage of water vapor at the interface layer will go further on. In the installation phase (phase 5), the aggregate starts to cool down, hence some microscopic cracks inside the particle are generated. In Phase 6, the water vapor starts to condense, creating a film of water at the interface layer. On the other hand, the water vapor inside the cracks also starts to condense. A part of the accumulated water at the interface is trapped inside the cracks because of traffic loads (in winter times as a consequence of frost-thaw cycles this process will even be more advanced). In phase 7 the outsource water e.g. rainwater starts to attack the aggregate and penetrate to the interface layer through the bitumen rupture points. Finally, (in phase 8) after a period of time the bitumen is stripped off from the aggregate surface and the rock also starts to disintegrate.

Based on this theory, water and other volatile constituents of the rock are the principal elements for causing the adhesion loss. If enough time is given to the aggregates for giving off their volatile constituents like water vapor and other gases, then this bond disruption between aggregate and bitumen could be less. The long storage phases prior to mixing with bitumen (inside the hot aggregate storage silos or section C) and after mixing with bitumen (HMA storage silos or section J) have great impacts on this phenomenon. In section C, where the hot aggregates are stored the possibility of occurring a reverse process is high. It means in these silos the hot aggregates are in a phase that they are still giving off their water content in form of water vapor. Therefore, the silos (which are closed systems) could be saturated from water vapor and as a result, when the temperature falls down the surrounding water vapor will condense and return to the aggregates as water. Accordingly, the aggregates coming out of the storage silos may have a wet surface prior to mixing with bitumen. This phenomenon causes a decrease in the adhesion bonding. In section J where the aggregates are stored after mixing with bitumen and other additives, the same phenomenon may also happen. However, this time in case of long storages, water will penetrate inside through the disruption points of bitumen. In all phases, the size of the aggregate is also a decisive factor and finer particles are more prone to this effect.

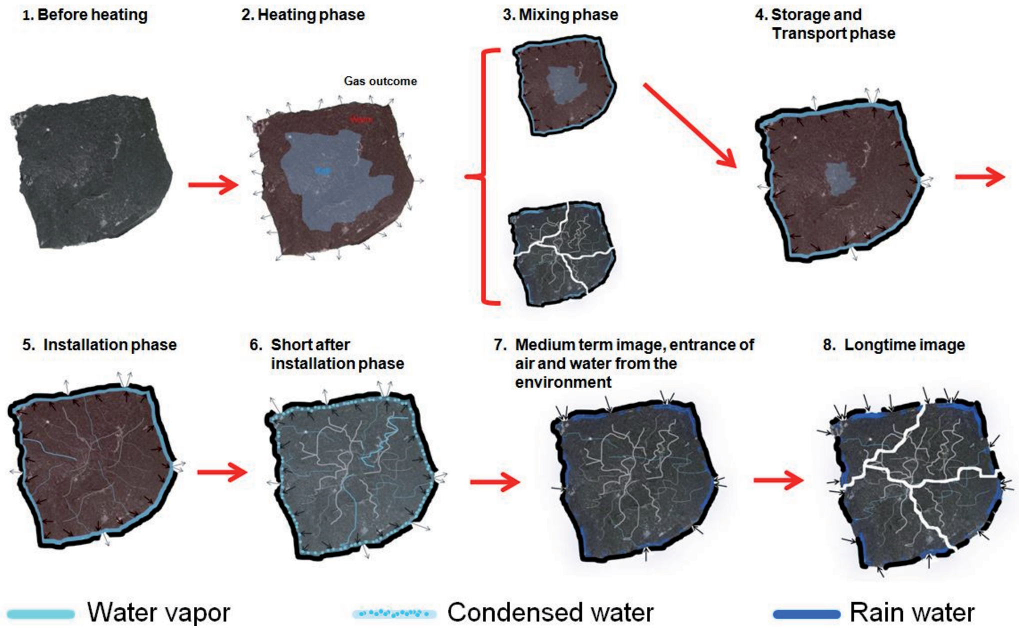


Figure 100 : Theory of water discharge leading to the reduction of adhesion between aggregate and bitumen

The principal component of this theory is the water content of aggregates. On the other hand, as discussed and proved before, the magnetic susceptibility of a sample has inverse relationship with its water content or loss on ignition value. It means, in order to understand whether the desired aggregate has high or low LOI value, the MAG value can be measured (which is much easier), whereas in special cases for obtaining 100% confidence the measurement of LOI is also recommended. Therefore, it seems that the two developed indices for rock quality determination might also determine the quality of asphalt. To prove this concept, further experiments are required.

In the next following chapters, various types of feasibility experiments are designed to evaluate:

- ✓ the effect of the developed indices (MAG/LOI) on the adhesion bond, and
- ✓ the accuracy of the mentioned theory.

To be able to identify the effect of LOI/MAG of the aggregates on bitumen-aggregate bond and the corresponding asphalt quality, different experiments are performed on various aggregate groups. The aggregates are categorized according to their MAG values namely high quality and low quality aggregates. Based on the results of the first stage of the studies (feasibility study of asphalt quality), a detailed study is performed on the quality of asphalt produced samples. To study the quality of asphalt samples (categorized by their LOI and MAG values) different experiments are carried out mainly based on existing asphalt DINs and NORMs. Then the results are analyzed and the thresholds of the indices are updated upon the asphalt quality requirements.

10 Feasibility studies for asphalt quality determination

The first feasibility studies regarding the two developed indices (LOI and MAG) and the “water discharge” theory are performed in this chapter. A systematic approach was planned to evaluate the influence of MAG and water content values of the aggregate samples on the adhesion force. The following experiments were designed in order to analyze different effects of the defined indices:

- ✓ LOI or water content experiments
- ✓ Pressure experiments
- ✓ Microscopic experiments
- ✓ X-ray tomography experiments
- ✓ Scanning Electron Microscope (SEM) experiments

The samples gathered for this phase of studies were basalt-andesite (from the same quarry as before). Based on their MAG and LOI values, they were grouped into two categories: high quality aggregates and low quality aggregates. The high quality samples had a MAG value of $6{,}00 \times 10^{-3}$ SI Units and LOI of less than 2% and the low quality samples had a MAG value of $2{,}80 \times 10^{-3}$ SI Units and LOI of 3,5%. The aggregate grain size fractions were selected based on the fractions practiced in a real asphalt recipe (in this research work a usual binder layer recipe was used).

10.1 Water content or LOI experiments

Main aim of this part of experiments was to specify if there is any relation between time, LOI and temperature. Experiments were applied on both types of samples to assess the relation between different parameters. To be able to model the situation of aggregates when exiting the dryer drum, the aggregates were heated between 200°C and 220°C. The heating time was also taken to be 120 minutes, which is more or less the time needed for the production of asphalt, transport and its installation on construction site.

As shown in figure 101, in a constant time of two hours, the LOI increases with increase in temperature. This rule holds true for both low quality and high quality aggregates. As an example, the graph for low quality aggregate is presented here. This experiment was carried out for several times with different aggregate types and different size fractions. The graph in figure 101 is based on an average value of LOI in different temperatures for the whole grain size spectrum.

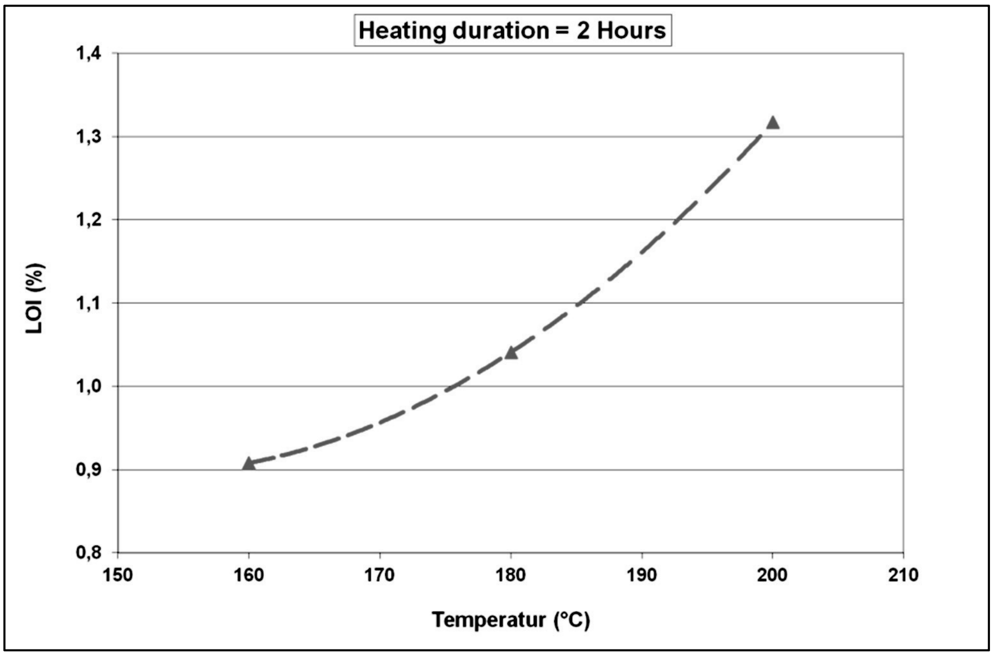


Figure 101 : Effect of Temperature on LOI of aggregates at a constant heating duration of 2 hours (low quality sample)

The variation of LOI and time with respect to the effect of grain size is shown in figure 102. In this experiment the temperature is kept constant (200°C) and the variation of LOI against time for two aggregate grain sizes has been depicted.

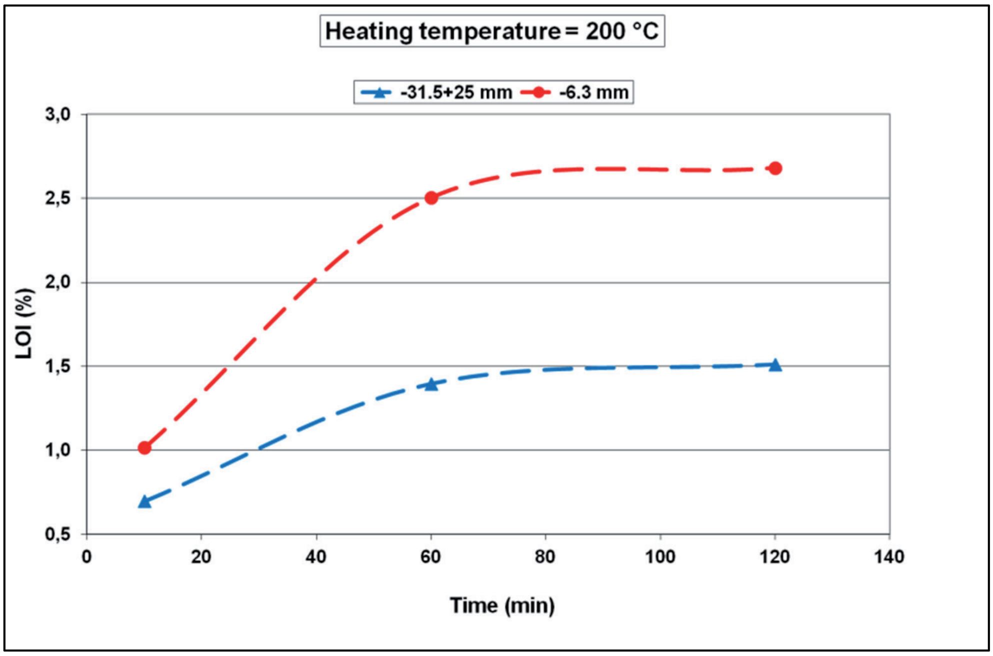


Figure 102 : LOI vs. time at a constant temperature of 200°C for different grain sizes (low quality sample)

As shown in the graph, with the size of grain aside and with a good proportion, in the first 60 minutes the water discharge rises. For smaller grains, the amount of water release is more. After about 60 minutes, the LOI will reach a constant value.

Figure 103 shows the effect of time and grain size on water discharge in a more detailed way. In this figure, the amount of LOI (in percentage) is converted to gram per minute and is plotted against different grain sizes. Since the effective time for water discharge is about 60 minutes (based on the different experiments), the experiment duration is also 60 minutes and the temperature is 220°C.

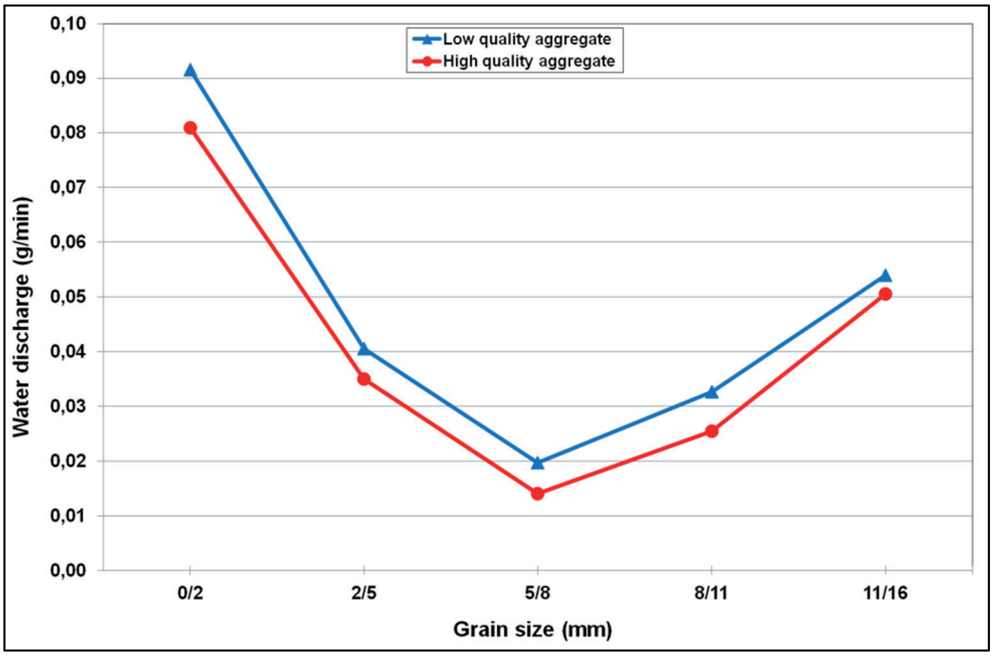


Figure 103 : Water discharge vs. grain size for different low and high quality aggregates (temperature=220°C, time=60 minutes)

It is clear that as expected the low quality material discharges more amount of water with respect to high quality material and this is true for all aggregate grain size fractions. On the other hand, the smallest grain size fraction, which is 0/2 mm, discharges the most amount of water. This shows the importance of the smaller size particles in asphalt which means they discharge the most amount of water within the asphalt production duration. To have a better imagination of the effect of 0/2 mm grain sizes on the asphalt quality, table 19 is presented. Analysis in table 19 is based on a typical asphalt recipe for binder layer which means the mass percentages of each size fraction is based on a usual binder layer recipe that is normally used by an asphalt company. Based on the calculations, although the 0/2 mm fraction in asphalt binder layer is about 30,5% by weight, but considering the surface area, it will occupy 75% of the whole aggregate grains surface area. Taking into account that the 0/2 mm fraction discharges the most amount of water and has the most shares in the total surface area of aggregate grains, the importance of the 0/2 mm fraction will be more realizable.

Table 19 : Share of different grain size fractions (in an asphalt recipe) with respect to total surface area of aggregates

Grain size (mm)	Mass fraction (wt. %)	Surface area of the aggregate grains (m^2/t)	Share in the total surface area of all aggregate grains (%)
0/2	30,5%	659	75%
2/5	16,5%	102	12%
5/8	7,0%	23	3%
8/11	14,0%	36	4%
11/16	32,0%	55	6%
	100%	875	100%

On the basis of our LOI studies in this part, the aggregate grains do discharge water at least in the first 60 minutes of their hot-preparation phase. This means they continue giving off water and gasses even though they are kept in a constant temperature. Therefore, in real practice when the aggregates come out from the dryer drum and then sieved and stored in the storage silos, they still do discharge water in form of gas or water vapor. The amount of the released water is a function of time, temperature, and grain size.

Figure 104 shows this effect in a photo. Although the sample was de-moisturized, but under further heating it lost its water in form of water vapor. The water vapor was condensed and appeared as a water drop on the inner wall of the glass. The condensed water will wet the aggregates again while they are stored inside the storage silos and will create further adhesion problems at the intersection layer between bitumen and aggregate surface.

(a)

(b)

Figure 104 : Water discharge of an aggregate, (a) prior to heating and, (b) after heating. The water vapor can be seen on the inner wall of the glass (left) and it turns shortly to water drop after condensation process (right)

10.2 Pressure tests

With this knowledge that the water-discharging phase of aggregates takes place in the first 60 minutes (even in constant temperatures), our priority is to know how much pressure this water vapor is able to produce. To evaluate the pressure exerted by the water vapor on bitumen layer, a set of new experiments were designed where with the use of an autoclave, the water vapor pressure produced by different types of aggregates was measured. The aggregates were placed inside the container (autoclave), afterwards the container was vacuumed and then heated up to the desired temperature (~200°C) and the pressure was studied in different times. The apparatus designed for the sake of pressure measurements may be seen in figure 105.

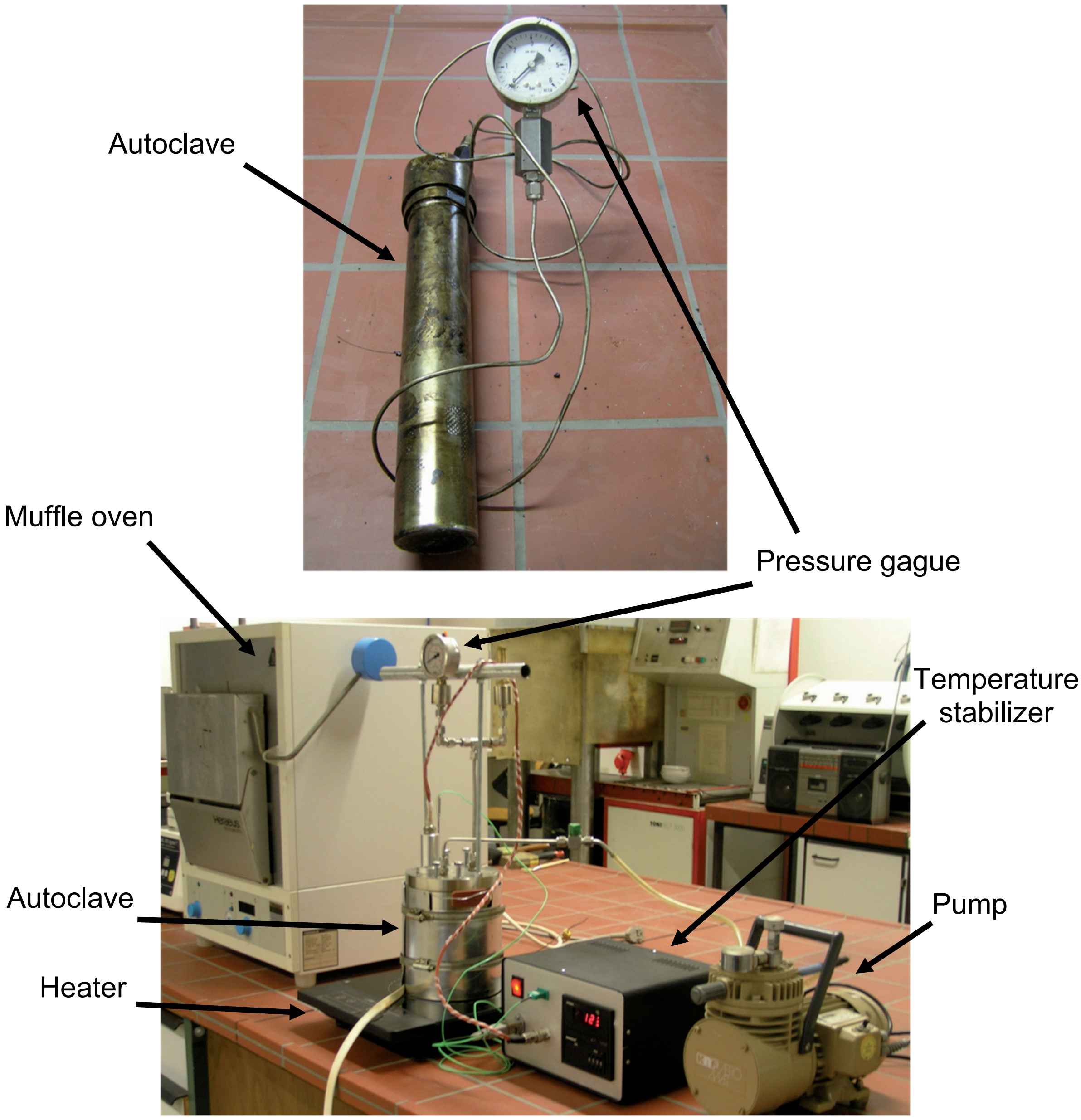


Figure 105 : Apparatus for pressure measurements produced by aggregates water vapor (when heated)

The pressure rises as the time goes by and the temperature increases (figure 106). The rise in pressure takes place in the first 120 minutes. It means when the aggregates are mixed with bitumen and then stored in the storage silos, they discharge water in form of water vapor. This water vapor will exert pressure in the first 120 minutes and after that, it (pressure) will gain a constant trend (it should also be noted that this phenomenon is independent from the aggregate quality and will occur in any case). The pressure is large enough to damage the bitumen layer around the aggregate and create craters on the bitumen surface. Craters could be assumed as the potential inlets through which water may penetrate inside under environmental conditions. According to our experiments, for this type of rock, the amount of pressure produced by the water vapor may vary from 3,40 Bar for high quality aggregates to 3,70 Bar for low quality aggregates. As expected the low quality aggregates produce more pressure with respect to high quality aggregates at a constant time.

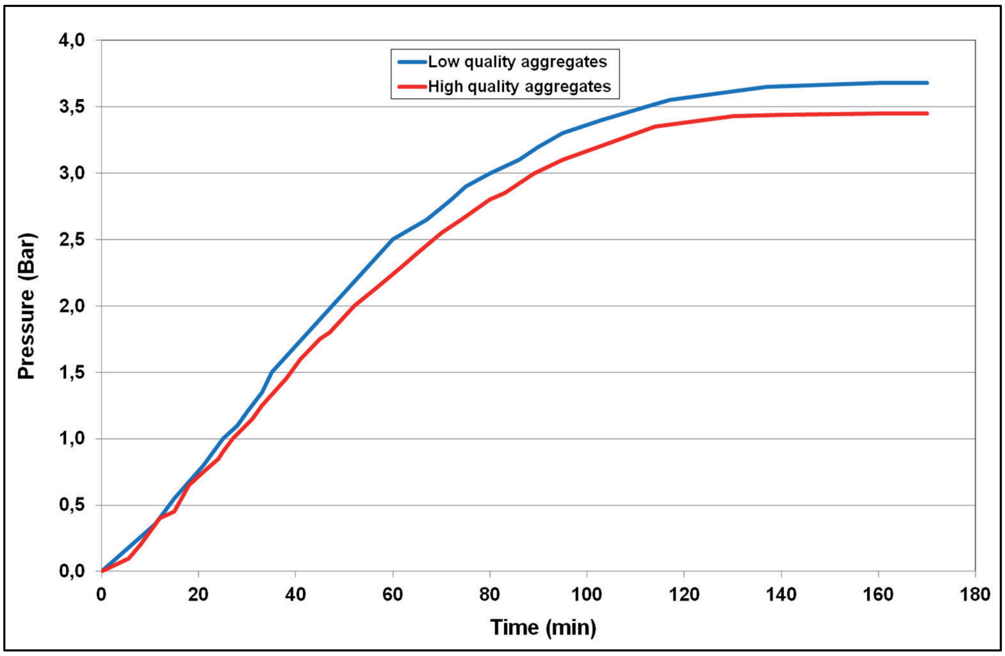


Figure 106 : Pressure vs. time for low quality and high quality types of aggregates (maximum temperature ≈ 200°C)

Based on our pressure experiments, the bitumen layer is damaged as the water vapor exerts pressure while forcing itself out through the surface of the aggregate. This phenomenon decreases asphalt quality as time elapses (independent from the quality of aggregates). If the quality of aggregates are not desirable or in other words if low quality aggregates are used for asphalt production, this rupture and damage to bitumen layer and consequent decrease in adhesion force between aggregate surface and bitumen will be even more, thus the quality of asphalt will be worst.

As a conclusion, all aggregates (regardless of their type, origin, and quality) have water in their structures. The aggregates will discharge this water in vapor form when heated (consequence of evaporation process) and the water vapor exerts pressure on its surroundings.

10.3 Microscopic experiments

In these series of experiments various types of aggregate sizes with different qualities were immersed in brown bitumen (therefore it is more recognizable) and then analyzed under a microscope and at the same time made some microscopic photos from them. The samples were placed in a plate full of water to evaluate the effect of water on the aggregates after they were immersed in bitumen and cooled down (figures 107 to 111).

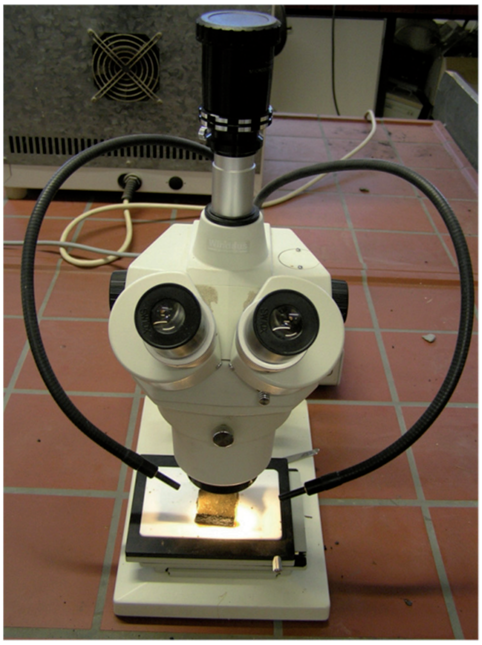


Figure 107 : Microscope used for studying the immersed aggregates in bitumen

Figure 108 : Surface of low quality aggregate after immersing in brown bitumen, plenty of air bubbles are recognizable

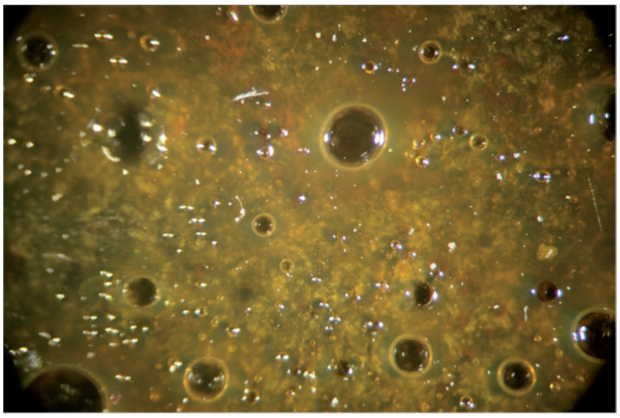


Figure 109 : Surface of high quality aggregate after immersing in bitumen, the numbers of air bubbles are reduced compared to low quality aggregates

Figure 110 : Aggregates immersed in water after mixing with bitumen and cooling down

Figure 111 : Stripping and separation of bitumen from aggregate surface. Bitumen is cooled down and the air bubbles under the bitumen film are visible. Latitudinal rupture of bitumen layer in the right photo is very obvious. The craters (which are formed as the result of water vapor vent) on the surface of bitumen layer are also noticeable.

The microscopic analysis of the samples also confirmed the LOI and pressure studies. The formation of air bubbles is completely visible under the bitumen layer. These air bubbles are formed as the consequence of water vapor trying to escape from the aggregate surface. The water vapor either forms air bubble underneath the thin bitumen layer, or passes through the bitumen film and forms a crater. Both cases will lead to an adhesion loss in the presence of water. The craters channel the surrounding water through and on the other hand, the air bubbles will burst or blow out under traffic load, leaving an empty void between bitumen and aggregate surface, which has the potential of being a perfect place for water accumulation. As time goes by, these voids may also be interconnected to each other creating micro channels for the passage of water. It shall be mentioned that since the air bubbles were formed between the bitumen layer and aggregate surface, when they blow out, they leave an empty space behind where the bitumen has no adhesion to the aggregate surface (these places are not wetted effectively with bitumen). This fact also has negative impacts on the adhesion loss, even in the absence of water.

10.4 X-ray tomography experiments

For this phase of experiments, an asphalt sample was made based on the aforementioned recipe (table 19). The sample was sent to computer tomography laboratory for further studies regarding its internal structure, which is not visible under normal conditions. Figures 112 to 114 show different stages of this experiment.

Figure 112 : Asphalt sample made with brown bitumen for x-ray tomography experiments

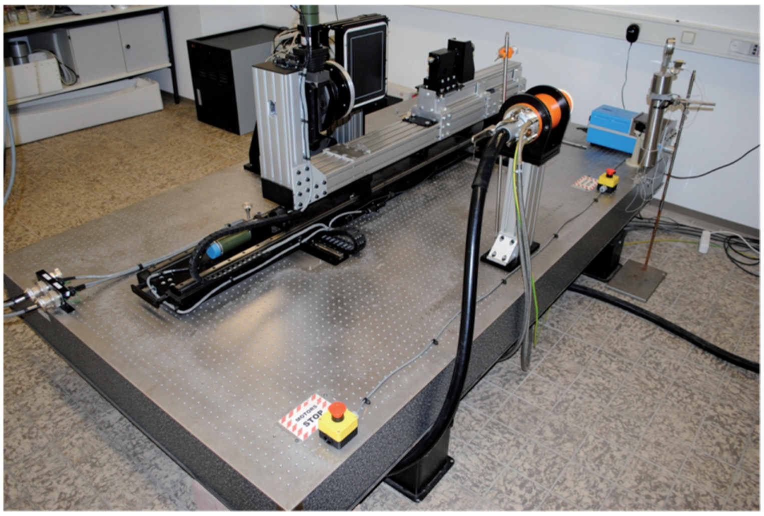


Figure 113 : Device for computer tomography

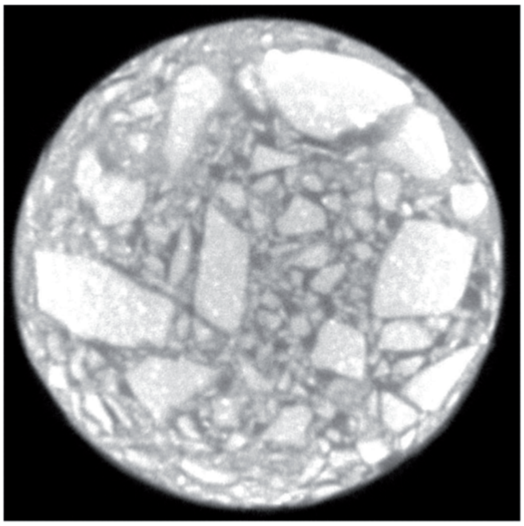
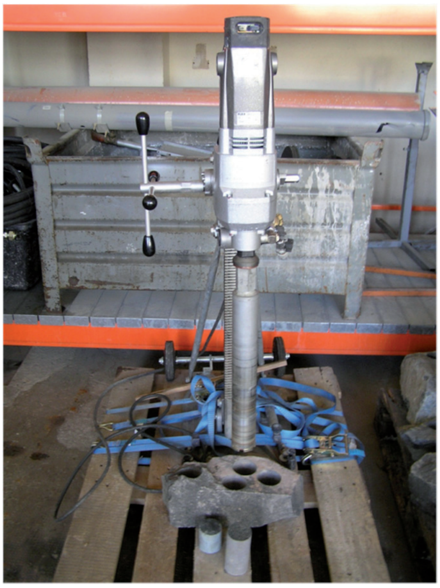


Figure 114 : A result from computer tomography of the asphalt sample (very bright=aggregates, bright=bitumen, dark=air bubbles or bitumen with air)

The existence of air bubbles were also confirmed by the X-ray tomography experiments. The air bubbles are distributed within the whole sample depth and were visible in different photos made at various depths of the sample.

10.5 Scanning Electron Microscope experiments

The Scanning Electron Microscope or SEM experiments were performed to study the exact effects of the pressure phase caused by water vapors. For this phase of studies, a borehole was drilled through the intact rock and then the core (with the use of sawing machine) was divided to several discs with equal heights. This experiment was carried out for both types of rocks: high and low quality. Figure 115 shows the different steps of producing the drilling core-disc samples.



(a)

(b)

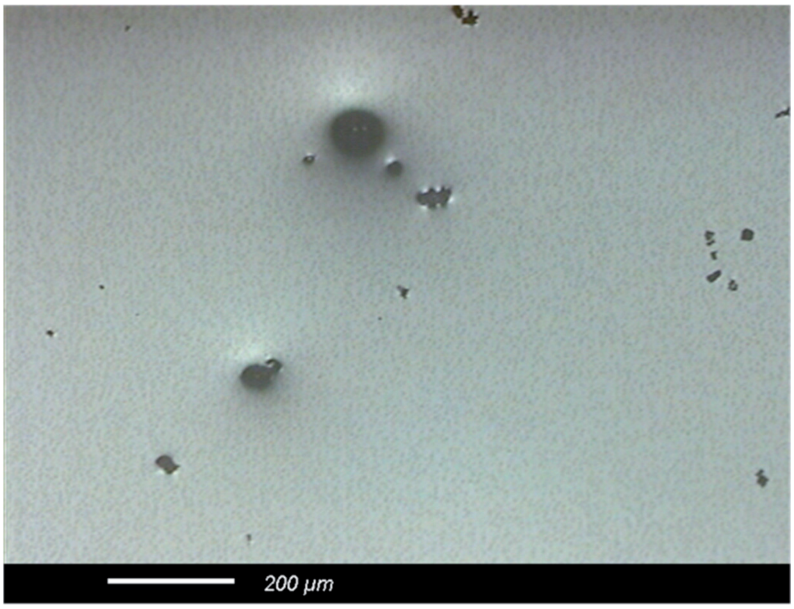
(c)

Figure 115 : Sample preparation for SEM studies, (a) borehole core-drilling machine, (b) sawing machine and, (c) final discs

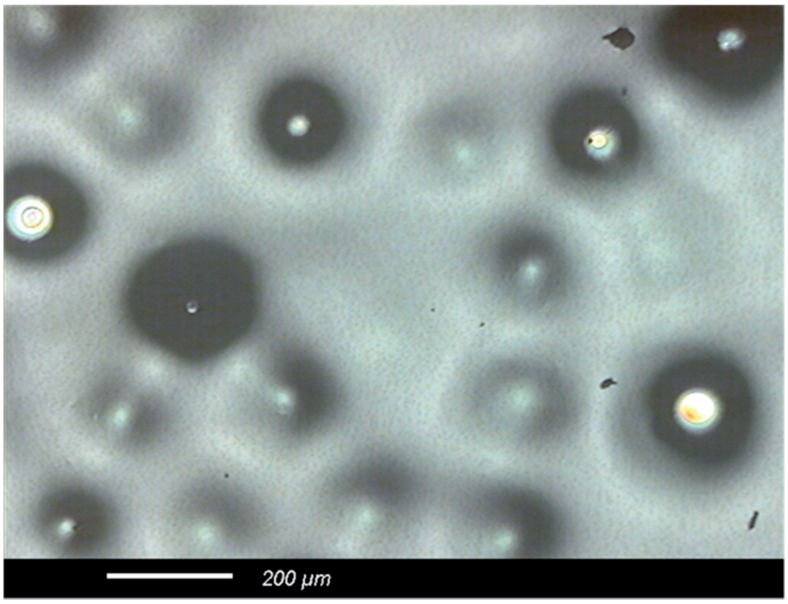
The produced discs from different types of rocks were mixed with bitumen and then placed under the SEM at different time intervals. Figures 116 and 117 show the photos made by SEM from the surface of the samples, 15 and 60 minutes after mixing with bitumen. The different surface-behavior of the high quality and low quality samples are clearly obvious in the photos.

From figure 116 (a) which corresponds to high quality samples after 15 minutes, it is clear that the vapor pressure has resulted in the formation of a few number of blisters and air bubbles. After 60 minutes (figure 116 (b)) it is visible that the number of air bubbles has increased; some bubbles could not develop fully and therefore burst, some craters are again filled with bitumen. The formation of hollow spaces and voids under the bitumen layer is clear. It is concluded that in case of good quality aggregates, the stability of asphalt samples that are made shortly after asphalt production will be higher than the samples that are made 60 minutes after production.

In figure 117 (a) which is related to low quality sample after 15 minutes, the vapor pressure has caused the formation of countless numbers of air bubbles, and the situation remains the same also for the 60 minutes samples. The air bubbles are in most cases fully developed and will burst. With the passage of time, the bitumen layer is damaged and the craters increase their sizes. As a result, the asphalt samples made out of low quality aggregates will have neither a high stability immediately after the asphalt production, nor one hour after production.

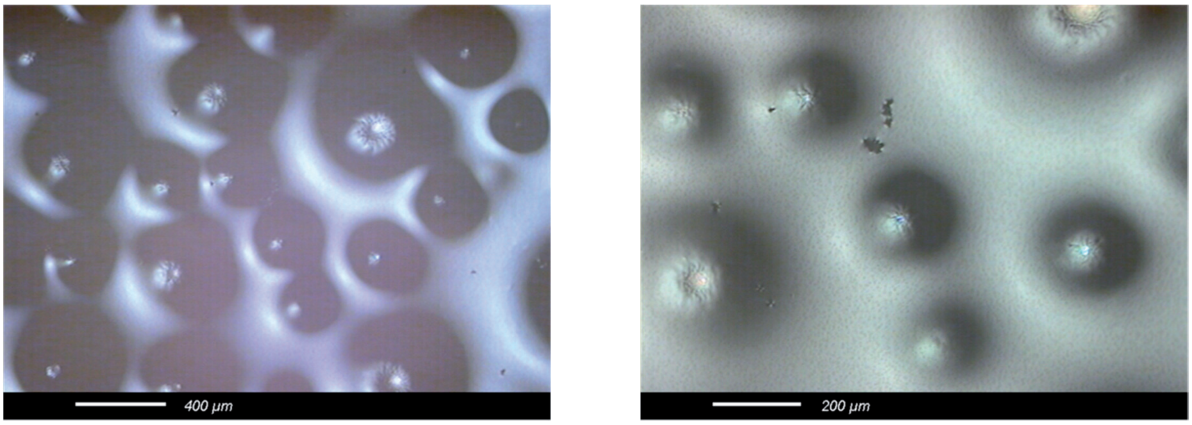


(a)

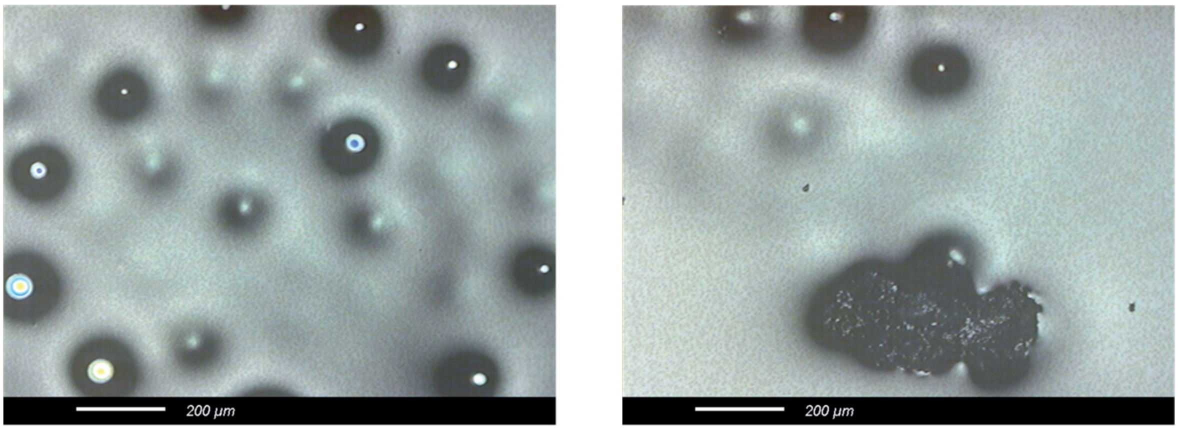


(b)

Figure 116 : Surface of high quality samples after mixing with bitumen, (a) after 15 minutes and (b) after 60 minutes



(a)



(b)

Figure 117 : Surface of low quality samples after mixing with bitumen, (a) after 15 minutes and (b) after 60 minutes

The observations of SEM studies complied fully with the results of other parts and confirmed specifically the analysis made by microscopic experiments.

10.6 Results and discussions

Various types of experiments were carried out to evaluate the accuracy of the mentioned theory. The fundamental assumptions of this theory were approved in different stages of the designed experiments. The water-vapor pressure is the key player in this theory and its influence was confirmed in all the above-mentioned experiments. All types of samples, regardless of their quality, do contain water and the emission of water vapor and other gasses begins (from center of aggregate toward outside) right after the sample has been heated and goes on until (at least) the first 60 minutes. The water vapor exerts pressure while getting out from the aggregate and this pressure will damage the thin bitumen layer and correspondingly reduces its useful life. In fact, the water vapor either passes through the bitumen layer or may not pass through and therefore forms an air bubble underneath the bitumen film. In case it passes through the bitumen layer, a crater is formed. Then it either remains as a crater or may also be filled again with bitumen shortly after the mixing process. If the crater remains, then the potential for water to penetrate through the bitumen layer and spread in the intersection layer will increase. On the other hand, if the air bubbles are formed, these bubbles have the potential to convert to hollow spaces underneath bitumen film and with time, they will be interconnected to one another and therefore create a void space for water accumulation. In case the air bubbles are burst (under environmental conditions e.g. traffic load), then the chance for water attack is still available. Therefore in either case (bursting or remaining of air bubbles), the bitumen layer has no real adhesion bonding with the aggregate surface. Based on the performed experiments the density of air bubbles formed on the surface of low quality aggregates are a lot higher, especially shortly after the mixing process. Other specifications such as LOI and water vapor pressure also confirms this issue (the LOI and water vapor pressure of low quality aggregates are higher than the LOI and water vapor pressure of high quality aggregates) and this is a crucial factor for further problems regarding the stripping of bitumen layer and consequently the reduction of asphalt quality. It shall be remarked that the low quality aggregates have lower value of magnetic susceptibility.

As mentioned before, the aggregates used for the asphalt production are basalt-andesite. When water penetrates through bitumen and to the interface layer, then it is in direct contact with aggregate surface. With time the aggregate surface is oxidized (in case low quality materials are used, then the aggregates are already altered and have an oxidized surface), therefore they form a hydrogen bond with the water layer and the water tends to wet the surface instead of bitumen. On the other hand the existence of oxygen and water in close contact to basalt surface at a high or basic pH (in this study the pH lies between 8,5 and 11) causes the oxidation of ferrous iron to ferric iron and its precipitatation as ferri-hydrite. The precipitation of ferrihydrite, which will also further oxidize to goethite (when the oxidation condition is maintained) leads to a more adhesion loss between aggregate surface and bitumen. The other issue that is notable, is the serpentinization process. As mentioned before, basalt is a mafic rock and the reaction of mafic rocks (rich pyroxene and olivine rocks) with water is called serpentinization. Serpentinization is an exothermic process, which increases the temperature up to 260°C. Constant contact of water with aggregate surface can lead to serpentinization of the aggregate which may create a temperature up to 260°C and this amount of temperature is high enough to damage the bitumen bonding and influences not only the adhesion but also the cohesion bond between bitumen-aggregate and bitumen-bitumen connection. All these issues will come together and result in the stripping of bitumen layer from aggregate surface. The other issue regarding serpentinization is the alteration effect. This phenomenon is a type of alteration leading to higher water content in the aggregate structure, hence reducing the affinity between bitumen and aggregate surface. In addition, Serpentinization also leads to formation of clay minerals, therefore this process not only causes a decrease in the durability of the aggregates but also results in swelling. Durability decrease and swelling increase of aggregates show their effects in swelling enhancement and stability loss of asphalt samples.

In the next two chapters, different types of asphalt experiments are designed in order to show the effect of this theory as well as the influence of the quality-defined indices (MAG and LOI) on the affinity problem and respectively on the quality of asphalt.

11 Detailed studies for asphalt quality determination

To assess the mentioned theory and to evaluate the effect of the determined quality indicators (LOI and MAG) in the field of asphalt industry, a series of laboratory asphalt experiments were designed. It is important to observe the influence of the aforementioned factors in practice, only then will the high degree of confidence be reached. Since the effect of time and temperature was significant in the feasibility studies, (prior to design of experiments) a brief measurement of time and temperature was carried out in the asphalt production plant. This information may help us in better design of the experiments.

11.1 Time-temperature measurements in HMA production plant

The process of HMA production was briefly explained in chapter 9. To be more exact, a time-temperature evaluation was carried out on the key sections of the asphalt production plant. Sampling was applied at the entrance and exit of the most important sections. The temperature as well as the retention time of aggregates in each sector was also measured.

Figure 118 shows a schematic view of a HMA plant and the corresponding locations where time and temperature measurements were carried out.

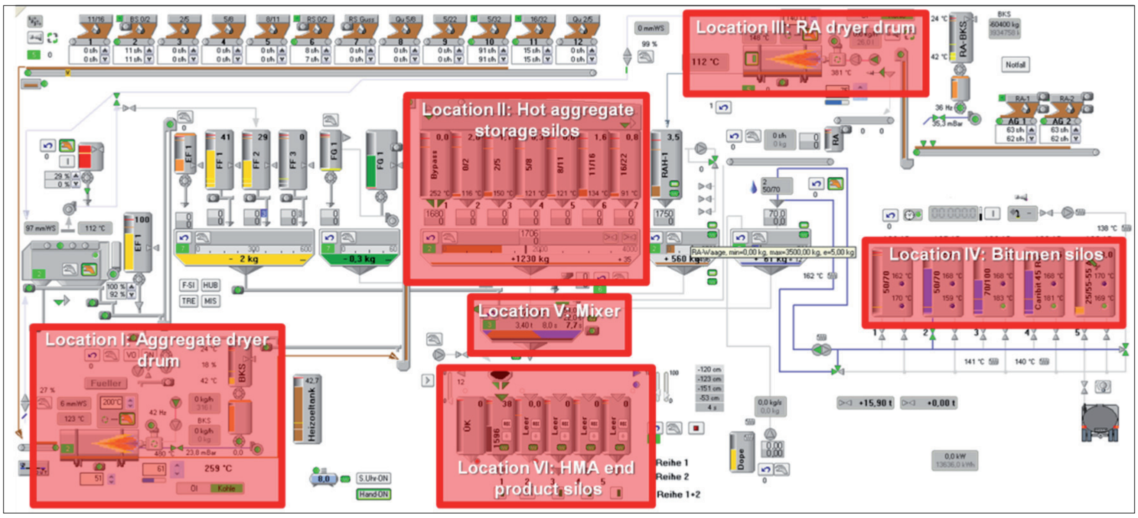


Figure 118 : HMA production plant and different sections for measuring retention time and temperature of aggregates [194]

The measurements of time and temperature were accomplished and the results can be seen in the table below.

Table 20 : Measured temperature and time in different sections of a HMA production plant

Location	Unit	Entrance temperature (°C)	Exit temperature (°C)	Retention time (min)
I	Aggregate dryer drum	Environmental temperature	250-320	6-7
II	Hot aggregate storage silos	< 250-320	178-280	minutes to hours
III	RA dryer drum	Environmental temperature	117-140	5-6
IV	Bitumen silos	Minimum temperature for being liquid	160-170	minutes to hours
V	Mixer	<178-280	175-220	1,5
VI	HMA end product silos	<175-220	175-206	minutes to hours

Since the temperatures of output material from the aggregate dryer drum (location I) had a significant importance, a short information (regarding the temperatures) was obtained from the responsible staff. Based on the direct information obtained from the staff, the temperatures of different layers are listed below:

Table 21 : Temperatures after the aggregate dryer drum based on information acquired directly from HMA plant staff

Asphalt layers	German equivalent	Explanation	Temperature (°C)
Covering layer	Deckschicht	without RA	220-230
Binder layer	Binderschicht	+30% cold RA	300-330
Base course	Tragschicht	+50-60% warm RA	280

In some cases (for the purpose of asphalt production), the recycled asphalt (RA) is also used. When so, then the RA (either warm or cold) is added to the hot fresh aggregates. In case the RA is cold, it is first stored in the RA storage silo and then added to the hot aggregate in the mixer. For this reason, the fresh aggregates are heated up to a higher temperatures such as 330°C in the dryer drum. When using warm RA, the RA is passed through the RA dryer drum and exits with an average temperature of 110-130°C, then stored in RA storage silo and is mixed with the hot aggregates in the mixer. In this situation, the fresh aggregates are heated to a lower temperature such as 280°C in the aggregate dryer drum. However, in both aforementioned cases (when using RA) the aggregates temperatures exiting the dryer drum are higher than the normal cases when no RA is applied (which is 220-230°C). The reason of applying higher temperatures (to aggregates in the dryer drum) when using RA, is to compensate the low temperature of RA and making the mixing process with bitumen and other additives possible.

Based on the obtained information regarding times and temperatures of different sections, it is now possible to move to design of experiments (DOE). The main aim of this part is to design the experiments in such an appropriate manner that it models the processes in the HMA plant in the best way.

11.2 Design of experiments (DOE)

The experiments were all followed by producing asphalt samples under DIN standards. The samples were prepared based on the "Marshall" method. To evaluate the stability and swelling of the asphalt samples, the following DIN/Standards and "Technical Test Regulations" were applied:

Table 22 : DIN and technical regulations applied for asphalt sample preparation and testing phase [196] [197] [198] [199] [200] [201]

Tests	DIN/Standard	Technical Test Regulations
Marshall stability & 48 hours swelling	DIN 1996 - part 9 DIN EN 1744-4 - Appendix A	TP Asphalt-StB - part 30 & 34
Indirect Tensile Strength (ITSR) & 72 hours swelling	DIN 1996 - part 9 DIN EN 1744-4 - Appendix A	TP Asphalt-StB - part 12

For each experimental design variant, at least three Marshall asphalt samples were prepared and for every alternative four types of tests were applied namely Marshall stability, 48 hours swelling (Marshall swelling), indirect tensile strength (ITSR) and 72 hours swelling test. This means for each set of experiments at least 12 asphalt samples were produced, but in most cases for accuracy reasons, more samples were prepared. The below-mentioned parameters were known as the most influencing factors on the quality of aggregates and that is why the experiments were so designed to assess the effect of these factors on the asphalt samples. The parameters are:

i. Magnetic Susceptibility (MAG)
ii. Loss on ignition (LOI)
iii. Time
iv. Temperature

The asphalt recipe applied to the experiments is as before (a usual binder layer recipe shown in table 23).

Table 23 : Recipe for asphalt samples

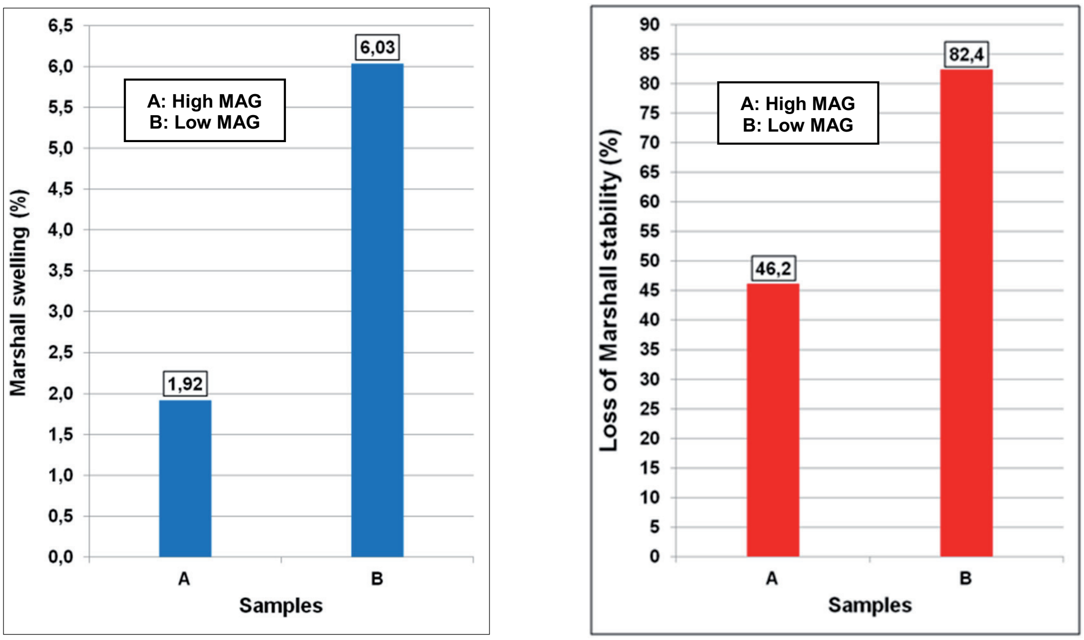
Grain size (mm)	Mass fraction (wt.%)
0/2	30,5%
2/5	16,5%
5/8	7,0%
8/11	14,0%
11/16	32,0%
Bitumen Shell 50/70	4,80%

In all asphalt samples, the “limestone” powder was used as aggregate filler. The Samples were (as before) categorized into two groups on the basis of their magnetic susceptibility values and LOIs. The first group was referred as high quality samples (produced from aggregates with an average MAG value of 6,00x10^{-3} SI Units and average LOI value of less than 2,0%) and the second group as low quality samples (made out of aggregates with an average MAG value of 2,80x10^{-3} SI Units and an average LOI value of about 3,0%). Since the LOI and MAG values have an inverse relationship with one another, studying the effect of one can also clarify the effect of the other one. Thus, the effects of the following influencing factors (on asphalt quality) were under our focus: magnetic susceptibility, time and temperature. The effects of the aforementioned parameters were studied by means of asphalt stability and asphalt swelling.

In all experiments, the sample preparation and testing phase were carried out based on DIN and TP-Asphalt requirements. In order to be able to model the preparation phase of samples in accordance with the reality (what really happens in a HMA plant), the aggregates were heated up to 200°C and then mixed with bitumen. Based on the measurements carried out in the plant (shown in table 20), in a normal process where the plant runs only by fresh aggregates and not by RA, the aggregates have an average temperature of 200°C prior to entering the mixer chamber. With respect to the design of experiments and in order to model the residence time of the finished asphalt product in the asphalt storage silos, different retention times (at 180°C) could also be given to the finished asphalt samples prior to their pressing phase by Marshall hammer. To model the RA case, where the normal aggregates are heated up to 330°C, the aggregate samples were also heated up to 320°C prior to mixing with bitumen.

11.2.1 Effect of magnetic susceptibility

The effect of magnetic susceptibility on the quality of asphalt was tested through Marshall swelling and loss of Marshall stability. The samples were prepared based on the normal asphalt production process, which takes place in a HMA plant and consequently in the construction site. This means in a normal situation, from the loading point of asphalt (by the trucks) to the construction location where the asphalt installation process takes place, it takes about 50-60 minutes. To model this effect, after the aggregates were brought to a temperature of 200°C, they were mixed with bitumen and then a retention time of 50 minutes in 180°C was given to the asphalt mixture prior to pressing phase (with Marshall hammer). Figure 119 demonstrates the experimental results.



(a) (b)

Figure 119 : Effect of MAG value (a) on Marshall swelling and, (b) on loss of Marshall Stability

The samples with low magnetic susceptibility had a swelling value of up to 3 times more than the swelling of the high MAG value samples. On the other hand the low quality samples (samples with low MAG values) had around 78% more Marshall stability loss comparing to high quality samples (samples with high MAG values).

11.2.2 Effect of retention time

To evaluate the effect of time on the quality of asphalt, different retention times were applied to the samples (with high and low MAG values) after the mixing phase. The effect of the retention/suspension time of the finished asphalt product in the asphalt storage silos, on the asphalt quality was then studied through Marshall swelling and Marshall stability loss of the samples. Effect of time was tested for both high quality (high MAG values) and low quality (low MAG values) samples.

11.2.2.1 High quality samples

The effect of retention time on the quality of asphalt samples was studied. For this purpose, asphalt samples composed of high MAG value aggregates were under our focus.

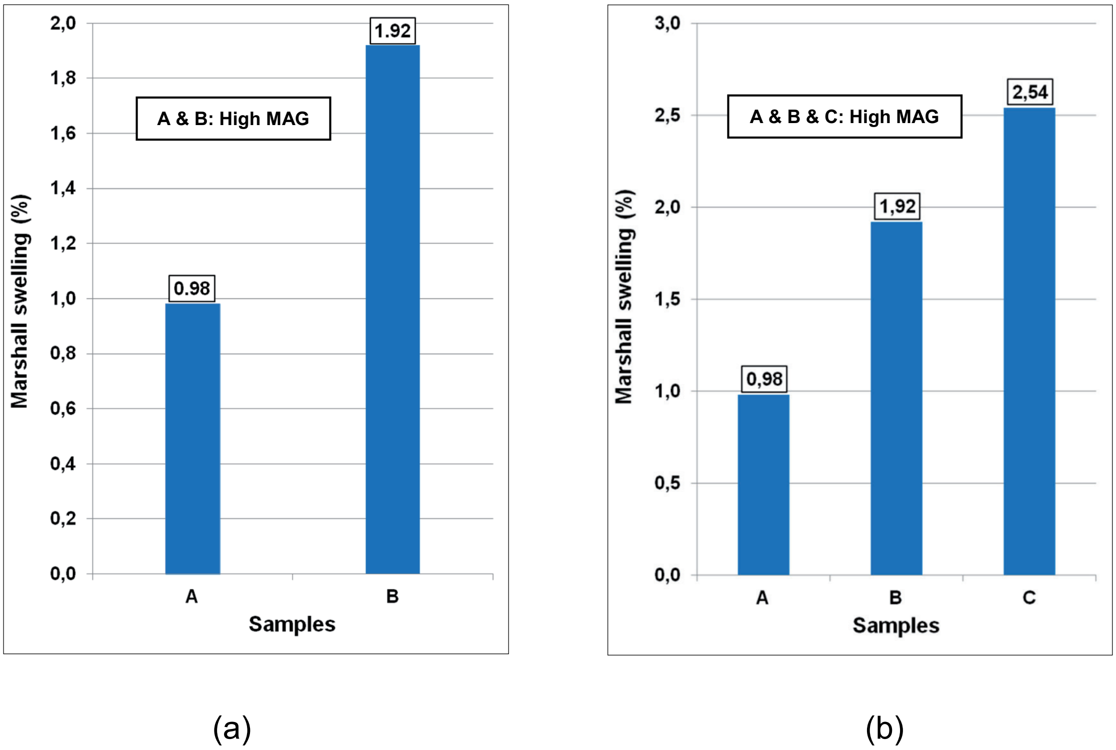


Figure 120 : Effect of retention time (of asphalt finished product in storage silos) on the swelling of asphalt samples made out of high quality aggregates: (a) two asphalt samples and, (b) three asphalt samples
(A) No retention time, (B) 50 minutes retention time and, (C) 180 minutes retention time

The results of the experiments can be seen in figure 120. It is clear that even though the samples were produced out of high quality aggregates (aggregates with high MAG values), the negative effect of retention time on swelling was still evident. In the first graph (a), samples with no retention time (A) and samples with 50 minutes of retention time (B) in 180°C temperature are compared with each other. A retention time of about one hour caused swelling growth of the asphalt samples. In the second graph (b), prolonging the retention time up to three hours (C) in 180°C has further increased the amount of swelling. In fact, after three hours of storage in 180°C, the swelling has increased up to 160%.

Figure 121 depicts the effect of retention time on loss of Marshall stability of high quality samples. Just as before, samples with no retention time (A) showed a lower stability loss compared to the samples with one-hour retention time (B). The one-hour retention time caused an increase of 58% in the stability loss of the samples.

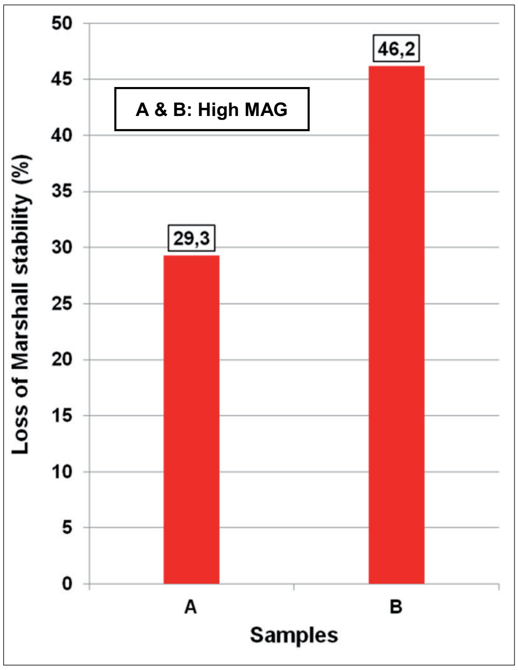
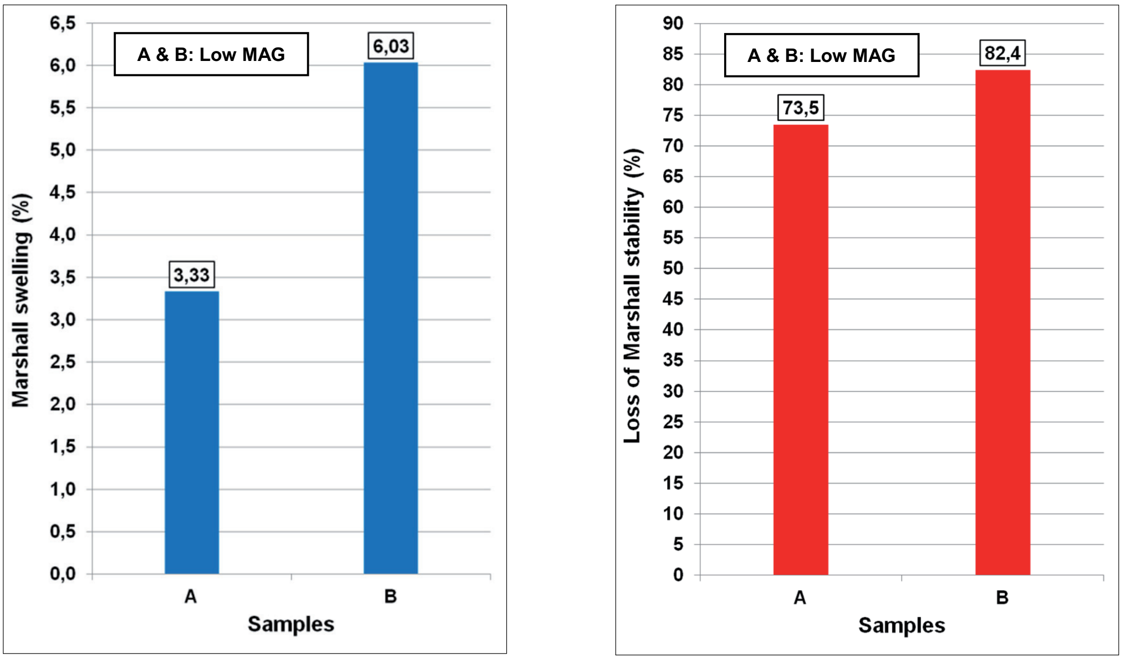


Figure 121 : Effect of retention time on Marshall stability of the high quality asphalt samples. Samples with no retention time (A) showed a better stability with respect to samples with one-hour retention time (B)

11.2.2.2 Low quality samples

Analogue to the experiments above, a series of experiments were also carried out on the low quality asphalt samples. The results of retention time on the swelling and stability of the samples are shown in figure 122.



(a) (b)

Figure 122 : Effect of retention time on (a) Marshall swelling and, (b) on loss of Marshall stability of asphalt low quality samples (sample A has no retention time, while sample B has 50 minutes of retention time)

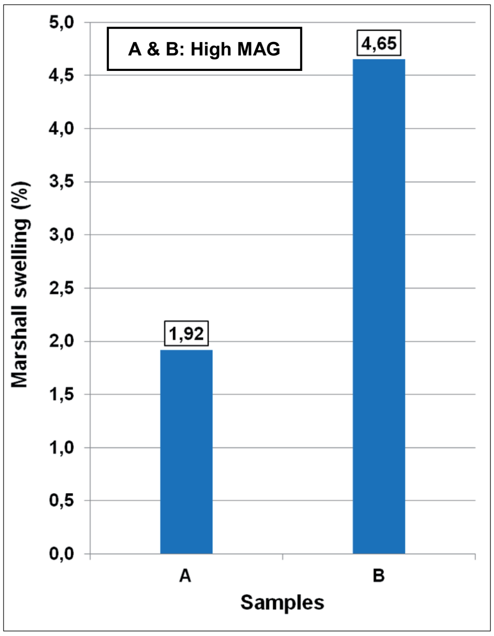
As in figure 122, the Marshall swelling and Marshall stability loss of samples with no retention time (A) is as predicted lower with respect to the samples which were exposed to a retention time of 50 minutes (B). This retention time of about one hour caused a swelling increase of approximately 80% (a) and a stability loss enhancement of 12% (b).

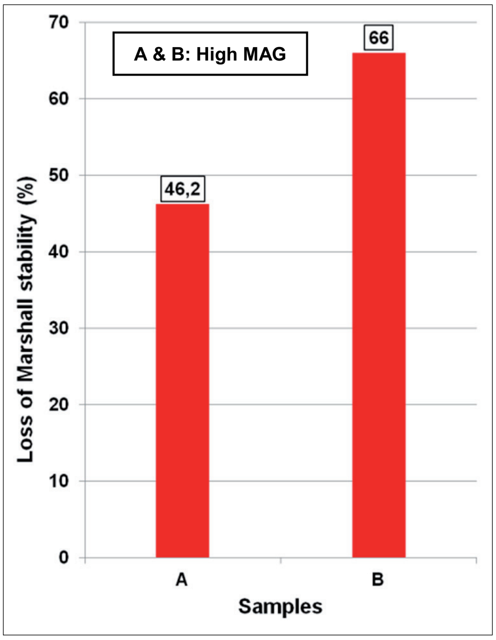
11.2.3 Effect of temperature

The effect of temperature was evaluated on both types of asphalt samples: high and low quality. This part was especially important because when RA was used as a part of material aggregate, then the fresh aggregates were over heated to compensate the low temperature of RA aggregates.

11.2.3.1 High quality samples

Asphalt samples made out of high MAG value aggregates were tested to assess the effect of aggregates temperature (prior to mixing with bitumen) on asphalt quality.
As clearly shown in figure 123, the rise in aggregates temperature, leads to an increase in both swelling and stability loss of samples. In section (a) of figure 123, sample A was prepared under normal condition, which means aggregates with 200°C were mixed with bitumen and then stored under 180°C for 50 minutes, whereas sample B was prepared with 320°C aggregates temperature. It means aggregates were heated up to 320°C and then mixed with bitumen and left in 180°C for 50 minutes and respectively pressed with Marshall hammer. The increase in temperature of fresh aggregates prior to mixing with bitumen caused a 142% increase in swelling factor. On the other hand in section (b) of figure 123, this increase in temperature from 200°C to 320°C leaded to a 43% enhancement in stability loss.





(a) (b)

Figure 123 : Effect of temperature on (a) Marshall swelling and, (b) on Marshall stability loss of asphalt samples with high quality aggregates: (A) samples with aggregate temperature of 200°C and, (B) samples with aggregate temperature of 320°C before mixing with bitumen

11.2.3.2 Low quality samples

The same trend as above held true for low MAG value samples, namely rise in temperature of aggregates prior to mixing with bitumen resulted in an increase in Marshall swelling as well as loss of Marshall stability.

11.3 Results and discussion

Various types of experiments were designed to investigate the effect of different influencing factors specifically, magnetic susceptibility, time and temperature, on the quality of asphalt.

The experiments of this phase completely approved the results of feasibility studies regarding the three aforementioned parameters. All the above factors have a great influence on the long-term durability of asphalt. The results of the detailed studies complied fully with last sections results. The microscopic, pressure, and SEM experiments all revealed the same fact. Indeed the facts that were observed in feasibility studies helped a lot in predicting the behavior of the asphalt samples under various experimental conditions.

Categorizing the asphalt quality on the basis of magnetic susceptibility has similar advantages as it had for railway ballast quality. The differentiation of aggregates based on their MAG values can help a lot in gaining a high quality and durable asphalt. Other factors i.e. temperature and time also play important role in the quality of asphalt. Increase in retention time of final product in the storage silos causes an increase in swelling and loss of stability of asphalt. The increase of aggregates temperature prior to mixing with bitumen also causes a great enhancement in swelling and stability loss of asphalt. In case of increase in retention time and temperature, the rise in swelling and stability loss is even more significant if low quality aggregates are used for production of HMA. This is another proof of the fact that in a HMA production plant, the quality control and quality assurance of the aggregates must be followed on the basis of magnetic susceptibility values or in special cases on the basis of loss on ignition values as well (which will be discussed in next chapter).

As a result of this phase, it is notable to mention that the quality of asphalt produced in a HMA plant is reduced because of the following points:

i. The application aggregates with low magnetic susceptibility values
ii. Overheating the aggregates in the aggregate dryer drum (especially in case of RA utilization)
iii. Long retention times in the aggregate storage silos (after the dryer drum and before mixing phase)
iv. Long retention times in finished asphalt product silos (after mixing phase)
v. Long transportation times from the HMA plant to the construction sites
vi. Increase in water absorption tendency of the aggregate surfaces as a result of overheating the aggregates in the aggregate dryer drum (overheating enhances the aggregate´s affinity for water. In other words overheating causes the aggregate surfaces to gain a greater affinity for water than bitumen binder (this issue was discussed in chapter 3 of this research work)

In the next chapter, a complimentary study will be carried out on the defined quality parameters, namely MAG and LOI. Subsequently their thresholds for having good quality asphalt in compliance to obligations and in full conformity to the state requirements will be determined.

12 Complimentary studies for asphalt quality determination

After about two years of implementing our proposed new aggregate quality index system, which was the measurement of magnetic susceptibility of the drilling fines, the quarry authorities reported the probable existence of a new anomaly. Based on the information reported by the quarry management, they were mining through a new anomaly where the magnetic susceptibility was relatively high but the quality of rocks were very low and they seemed extremely altered. To ascertain the possibility of alteration, they measured the loss on ignition value and also produced asphalt samples out of these types of rocks. The measured LOI values were very high. On the other hand, very high loss of stabilities as well as large swelling percentages were recorded. This problem was reported to us and based on assumption of the existence of a new anomaly, a detailed complimentary study was carried out. To understand and recognize the new challenge faced by our industry partner, a set of novel experiments were designed. The experiments were carried out in three phases, namely reconnaissance, identification/justification and threshold determination phases.

12.1 Phase I: reconnaissance

In the first step of this phase, in order to check the reproducibility of the results that were reported by the industry partner and to make sure that the new anomaly exists, a set of experiments were arranged by means of:

- ✓ Production of asphalt samples (where the swelling and stability loss were under concentration)
- ✓ Microscopic thin/polished section studies
- ✓ LOI/MAG measurements
- ✓ X-Ray Diffraction analysis

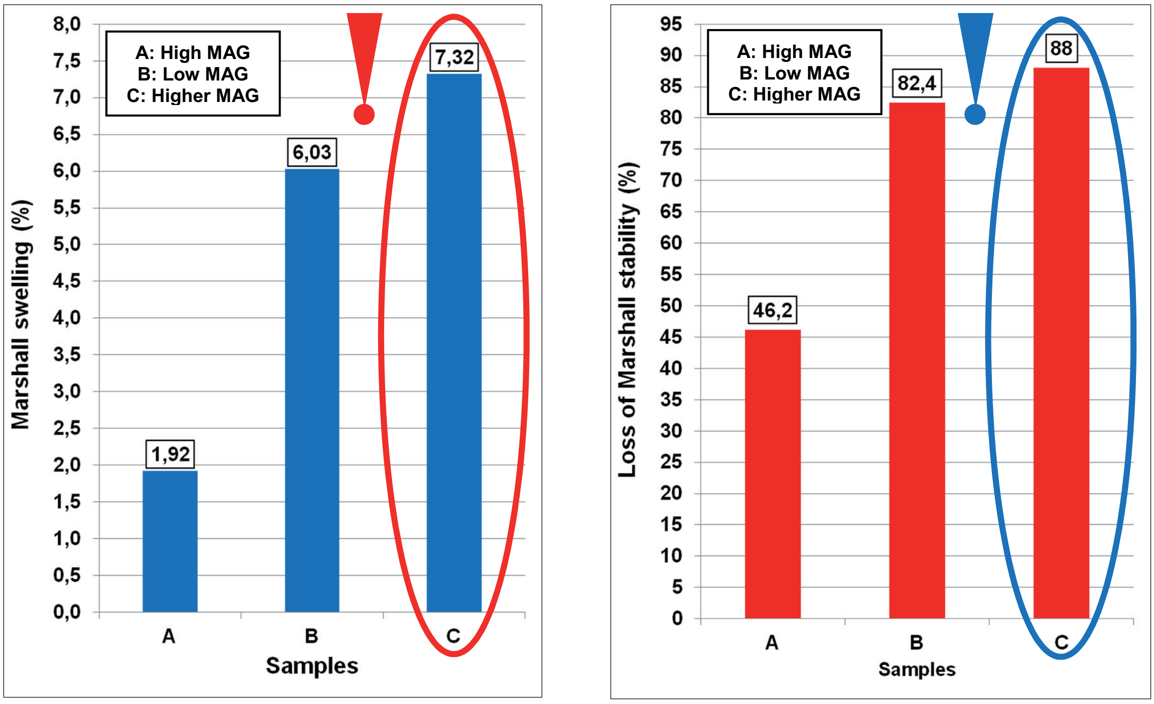
Sampling was done from the blasted problematic muck-piles. Afterwards the grab samples were prepared (crushed, milled, and categorized) for performing asphalt tests, microscopic studies, LOI/MAG measurements, and X-ray Diffraction analysis. In the next sections, the experiments and their corresponding results are presented.

12.1.1 Asphalt experiments

The same asphalt recipe and bitumen type (as before) were used for the asphalt experiments. The MAG values of the new samples were relatively high as reported (almost 8,00 x 10^{-3} SI Units). The results of the experiments are shown in figure 124.

Figure 124 (a) presents the Marshall swelling values of the samples. Sample A had a high MAG value with low swelling and sample B had a low MAG value and a high swelling. On the other hand, sample C (the new sample) had a relatively higher MAG value than sample A. Thus, based on the influence of MAG value on the Marshall swelling which was discussed in chapter 11, it was expected to gain a low swelling percentage for the new sample C. In fact, the value of swelling for sample C was estimated to be lower than or equal to the swelling value of sample A. However, the results showed something else, which was interesting. Instead of obtaining a swelling value smaller than or equal to 1,92%, an amount of 7,32% was gained from the experiments perused with the new muck-pile aggregates (which had a higher MAG values). Surprisingly, the swelling value was even greater than the swelling of low MAG value samples.

This trend was also confirmed in figure 124 (b). Notwithstanding the fact that sample C had the highest MAG value but interestingly it had the highest stability loss as well, which did not satisfy the former results. Based on our previous findings, MAG value can have a positive or negative effect on the stability loss, which means the higher the MAG value the lower the stability loss and vice versa. However, it did not hold true for the new muck-pile samples. The new sample (C) had the highest MAG value therefore, it was predicted to gain a low stability loss for it (at least smaller than or equal to stability loss of sample A) but in reality, its stability loss reached the highest value among all three samples. Stability loss of sample C was even higher than sample B, which was produced from low MAG value aggregates!



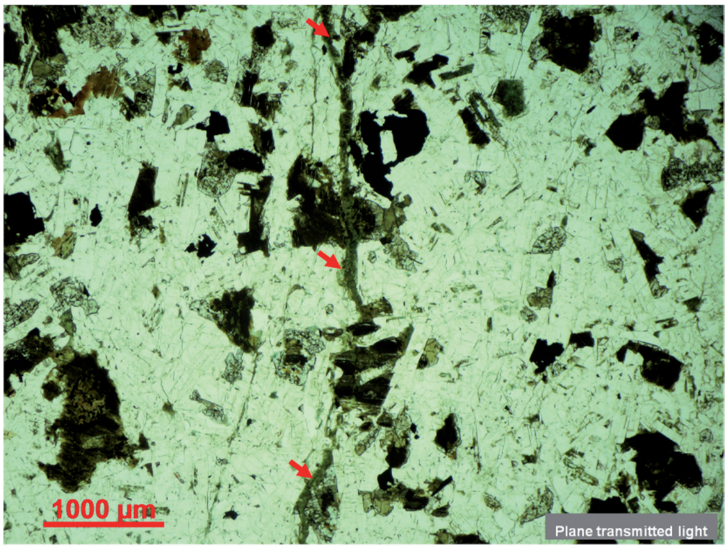
(a) (b)

Figure 124 : Effect of MAG value on (a) Marshall swelling and, (b) Marshall stability loss of the asphalt samples (including the new asphalt sample (C) made of aggregates with higher MAG values)

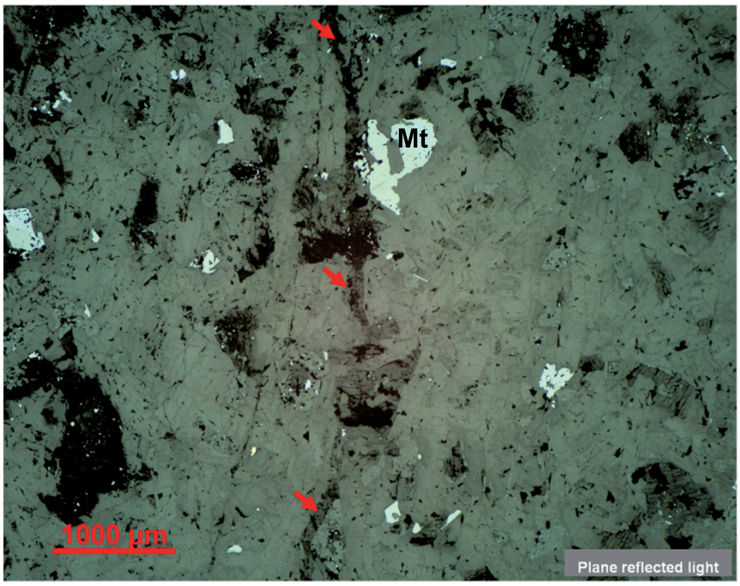
12.1.2 Geological and microscopic thin/polished section study

To obtain more information regarding the mineral assemblage of the new samples, mineralogical and thin/polished section microscopic studies were performed on the samples. The results of the microscopic studies are depicted in figure 125.

The information gained from the mineralogical and microscopic studies showed that the new samples have under gone the chloritization and serpentinization processes, which are both known as a type of alteration. As a result of these types of alterations, pyroxene and olivine groups are altered and minerals like serpentine and chlorite are formed. Nevertheless, the magnetite content of the samples remains either constant or even increases. This was the main reason of getting a high MAG value in spite of high degree of alteration of the new samples. In figure 125 (a) the chlorite band is pretty clear and in section (b) the fresh magnetite crystals are also obvious. The existence of chlorite and serpentine as well as the fresh magnetite crystals in (microscopic photos of) the samples confirmed our primary geological evaluations.



(a)



(b)

Figure 125 : Microscopic photo of thin/polished section in (a) transmitted light and, (b) reflected light. The chlorite band is completely clear in both photos. In Photo (b) the magnetic crystals are also visible (brownish grey color and marked with “Mt”)

Chlorite and serpentine are both phyllosilicate minerals that (by some classifications) are categorized under clay minerals. This is why asphalt samples made from these aggregates had a high swelling and large loss of stability values although they revealed a high MAG value from themselves.

12.1.3 Loss on ignition/magnetic susceptibility study

A study for LOI and MAG values was carried out on the new samples. For this purpose, a number of LOI tests (on samples with grain size smaller than 1 mm) and MAG value measurements (on powder samples or borehole cuttings) were performed to gain accurate values for the LOI and MAG. The average value of the readings was taken as the representative value for LOI and MAG. The amount of loss on ignition of the new samples was about 3,5% and the magnetic susceptibility value was ca. $7{,}50 \times 10^{-3}$ SI Units, respectively.

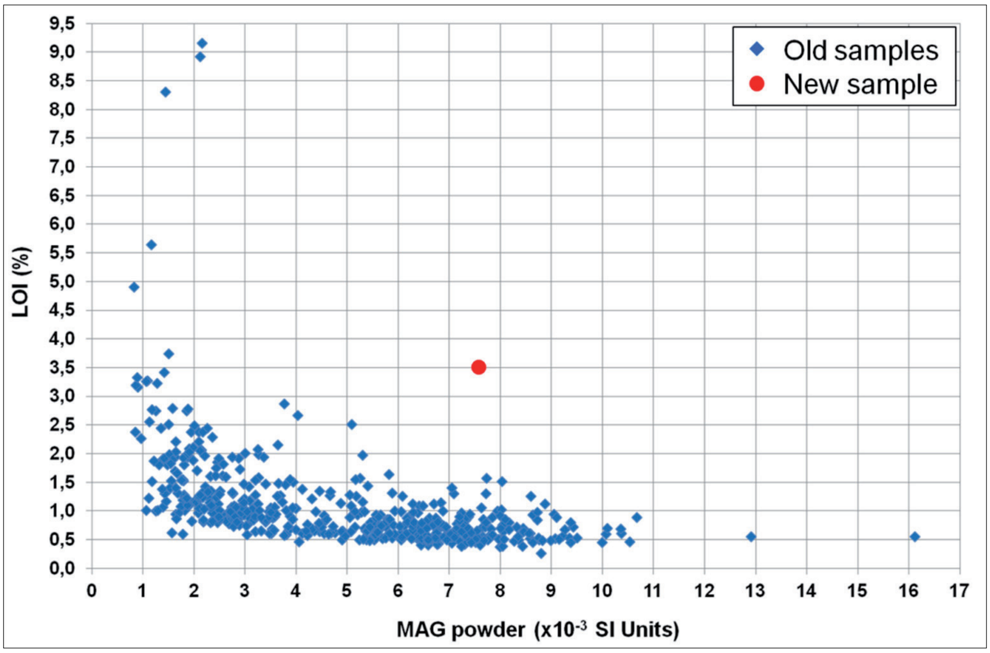
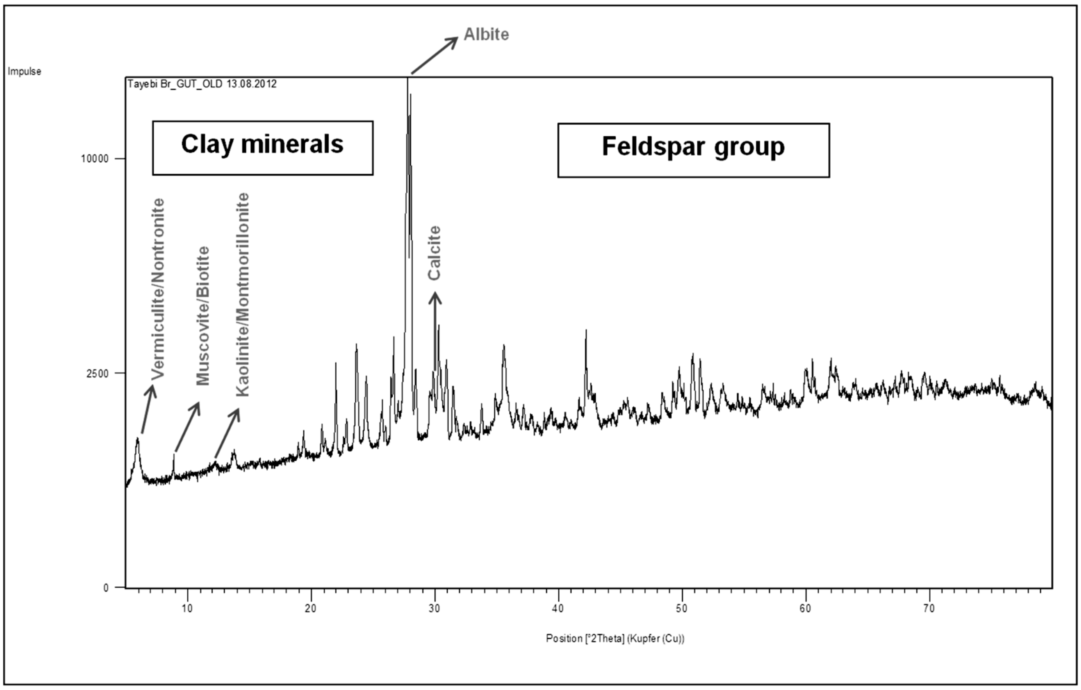


Figure 126 : The location of the new sample (red point) in LOI-MAG graph of the quarry

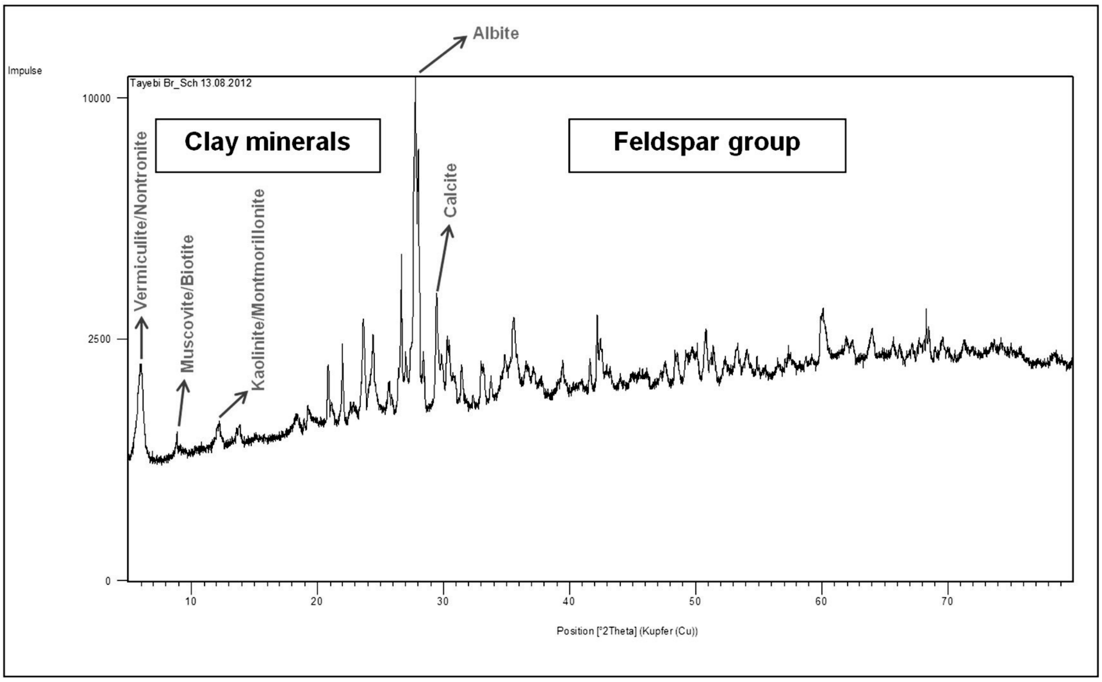
Figure 126 shows the location of the average MAG and LOI value of the new sample within the general LOI-MAG graph of the quarry. It is clear that the LOI and MAG value of the new sample completely lies outside the former measurements. The measurements on the old samples in figure 126 were accomplished on more than 500 different samples gathered from various locations of the quarry. None of the old measurements shows the existence of LOI and MAG value in the range of the new sample. The MAG-LOI analysis also confirmed that the mining operation was confronted with a new anomaly.

12.1.4 X-Ray Diffraction studies

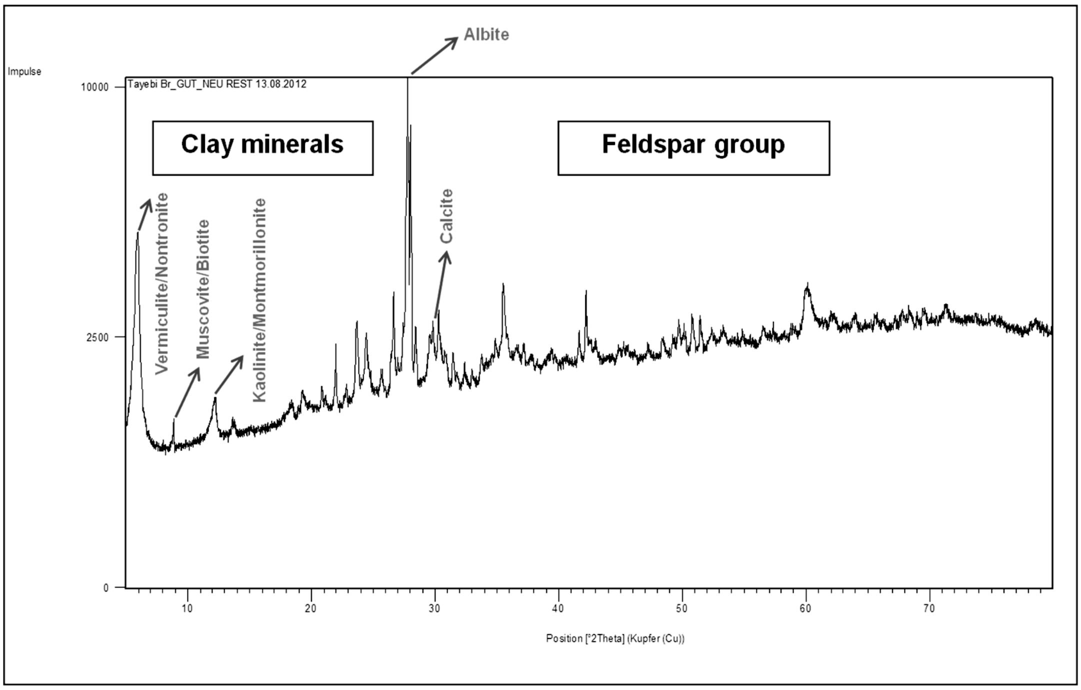
To recognize the different mineral assemblages and their phases in a more precise manner, the samples with low MAG values, high MAG values and the new samples (with higher MAG values) were sent to X-Ray Diffraction (XRD) laboratory. The results of these investigations were very interesting. Figure 127 presents the results.



(a) Old sample with high MAG value and low LOI value



(b) Old sample with low MAG value and high LOI value



(c) New sample with high MAG value and high LOI value

Figure 127 : Results of the XRD on (a and b) the old and, (c) on the new samples (the vermiculite/nontronite content of the new sample is significantly higher than the other two samples)

The results of the XRD studies of the samples revealed the existence of a higher content of clay minerals in the new sample. As shown in figure 127, the amount of clay minerals in the new sample (which simultaneously has high MAG and LOI values) is more than the two previous samples (first sample (a) had a high MAG value but low LOI value, the second sample (b) had low MAG value but high LOI content). The amount of nontronite and vermiculite is extremely increased in the new sample (c). Vermiculite and nontronite are both phyllosilicates and are categorized under clay minerals group. Vermiculite has four molecules of water in its crystal structure and nontronite may take up to “n” molecules of water. Therefore, this is exactly the reason why the new sample had an extraordinary amount of water in its structure. The extent of other clay minerals such as muscovite, biotite, kaolinite and montmorillonite are little in the new sample.

It is also clear from figure 127 that the amount of clay minerals (especially vermiculite and nontronite) in the first sample (a) that had high MAG and low LOI values, are lower than the second sample (b) that had low MAG but high LOI values. This is another confirmation for the fact that why the samples with high MAG values (or high quality samples) had lower amount of LOI than the samples with low MAG values (low quality samples).

12.1.5 Results and discussions

From the results of the primary asphalt experiments, geology/microscopic studies, LOI/MAG measurements as well as XRD analysis, which were applied with the aim of evaluating the reported information from our industry partner, the basic concept of the existence of a new anomaly was confirmed. Different aspects and characteristics of the new anomaly was studied in detail and on this basis a new concept was constructed which will be described in the next phase.

12.2 Phase II: Identification and justification

After obtaining the preliminary information about the new anomaly from phase I, the studies regarding this anomaly entered to its next stage, phase II. Sampling, LOI/MAG investigations, XRD studies, and natural weathering tests were applied in this phase to gather more information about this new altered zone.

12.2.1 Sampling

The main aim of this stage of the studies was to evaluate the extent of the confronted anomaly in the quarry. For this reason, a vast sampling program was planned. Sampling was performed from all benches, however our sampling concentration was mainly on the desired point (the new discovered alteration zone) and other probable alteration and inhomogeneous zones.

Figure 128 displays the location of sampling points. Area "E" in this figure shows the neighborhood of the new anomaly, which was located on 3rd bench in the southern part of the quarry. More or less 100 single hand-piece (grab) samples were gathered for further investigations.

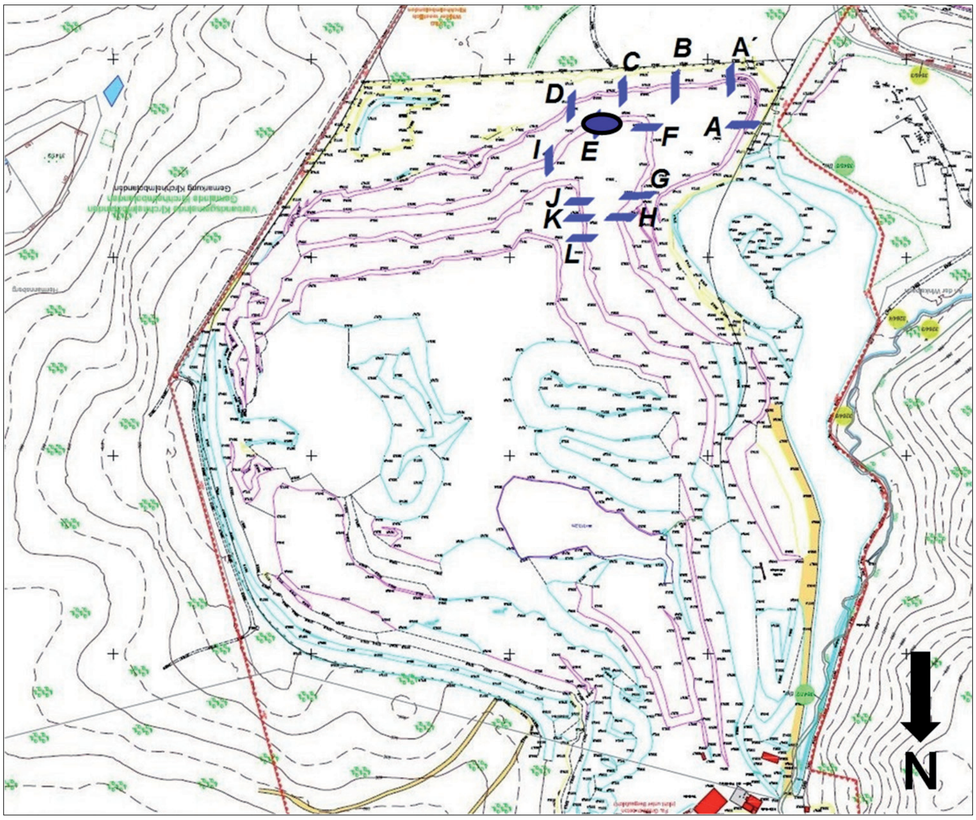


Figure 128 : A schematic vies of sampling locations with concentration on point E (new anomaly) and other probable altered zones and geologically heterogeneous areas

12.2.2 Loss on ignition and magnetic susceptibility measurements

The samples gathered from the quarry were prepared for LOI and MAG value measurements. Figure 129 shows the location of new samples with respect to old samples in a LOI-MAG diagram. It is obvious that there are some “outlier” points such as D, E and F that are completely out of the concentration of other old and new samples. Theses samples have high MAG values and at the same time contain high volatile contents. This is due to the type of alteration process that occurred in these locations. Having a look at the map shows that point F lies in the vicinity of point E at the same bench and point D also lies close to point E but at a higher bench. In other locations like A, B or J and K there was no evidence of the same alteration process. For example locations A, B and K had high quality rocks and point J revealed the normal alteration as before (high LOI value and low MAG value).

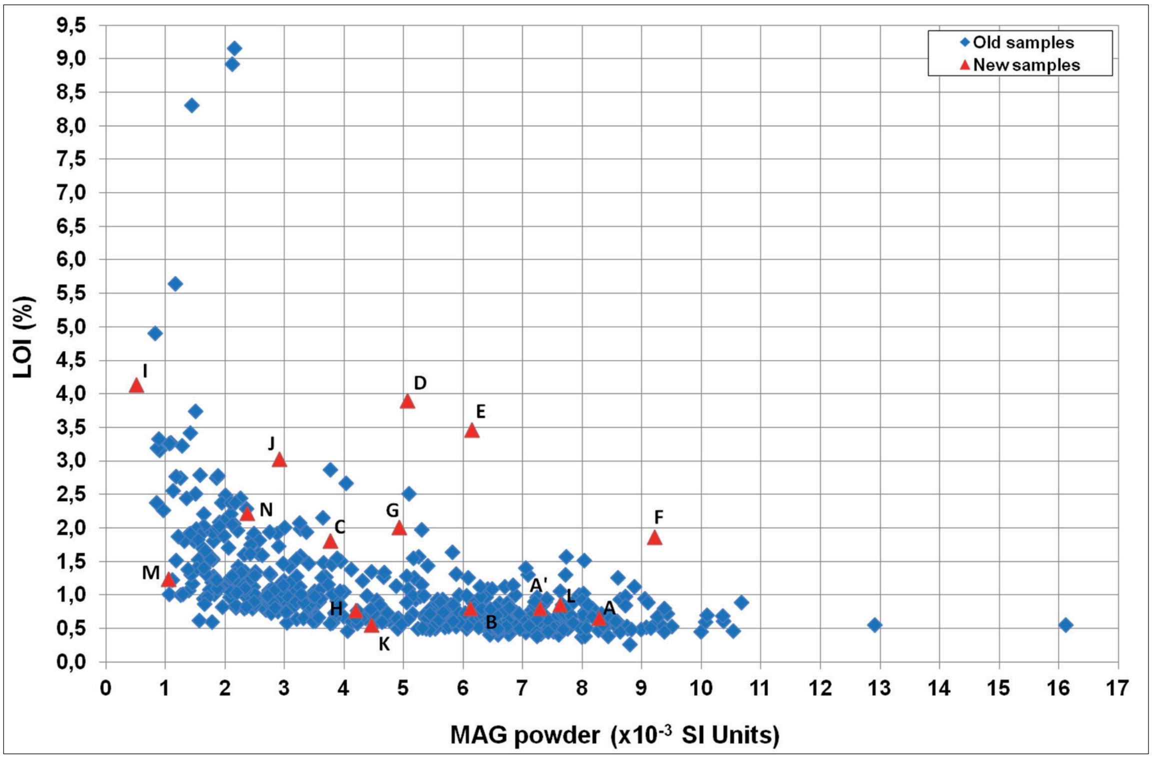


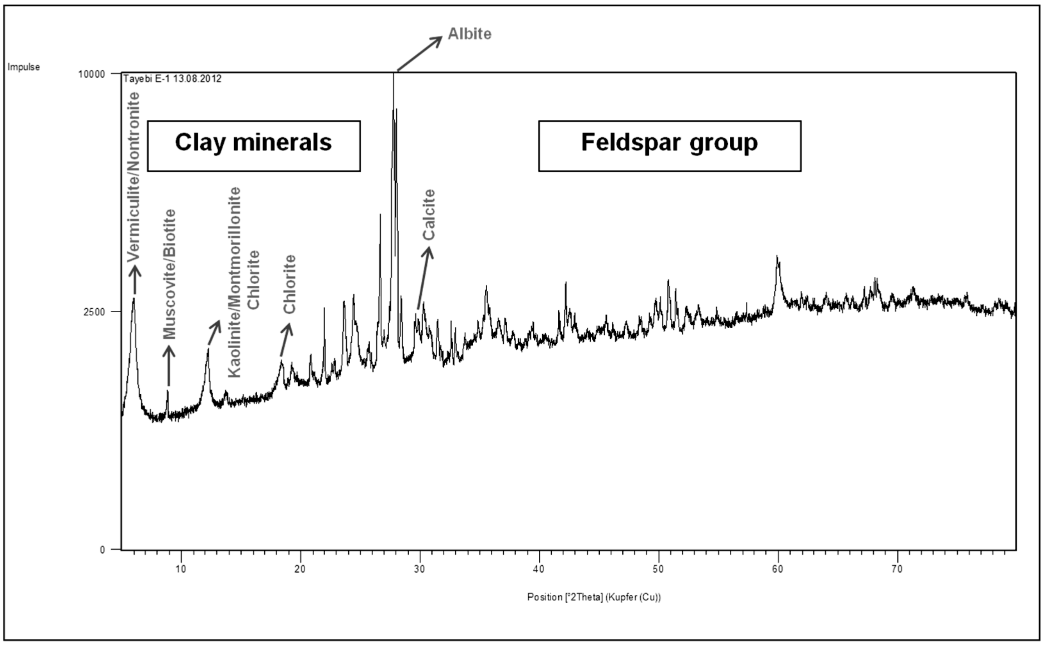
Figure 129 : LOI vs. MAG diagram showing the position of the new samples with respect to old samples (D, E and F are outliers)

12.2.3 Geological and microscopic studies

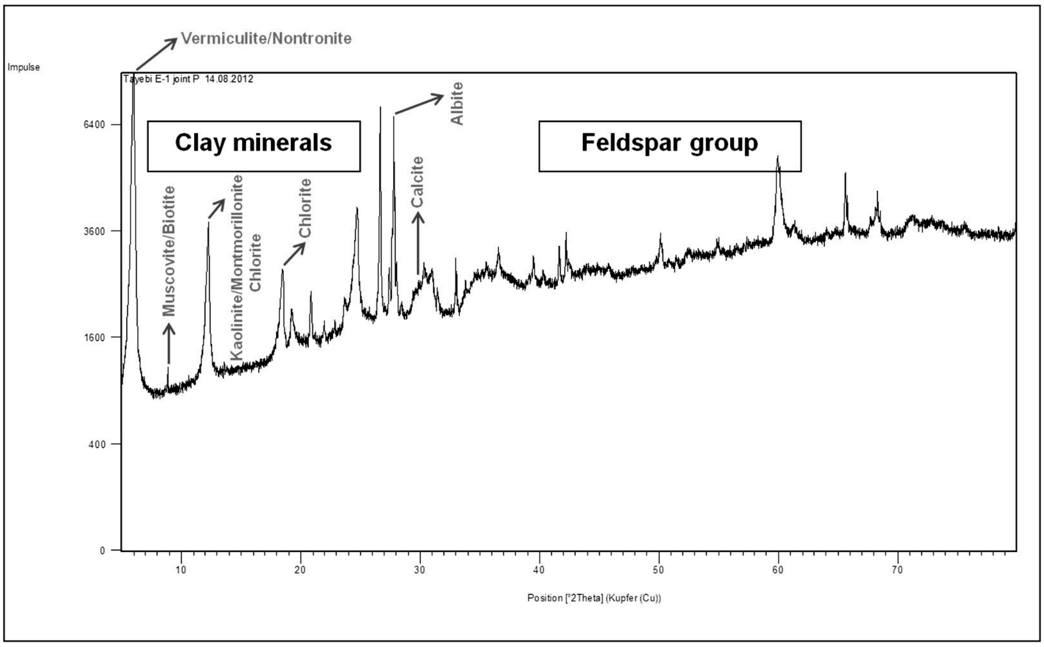
Similar to the previous studies, a geological and thin/polished section microscopic investigations were performed on the samples (with concentration on samples from outlier points D, E and F). The results were similar to the results obtained from our previous microscopic studies in this chapter (section 12.1.2). As expected, these samples were affected by chloritization and serpentinization alteration process. They had high content of water and volatile components and high magnetic susceptibility values due to the existence of fresh magnetite crystal in them.

12.2.4 XRD studies

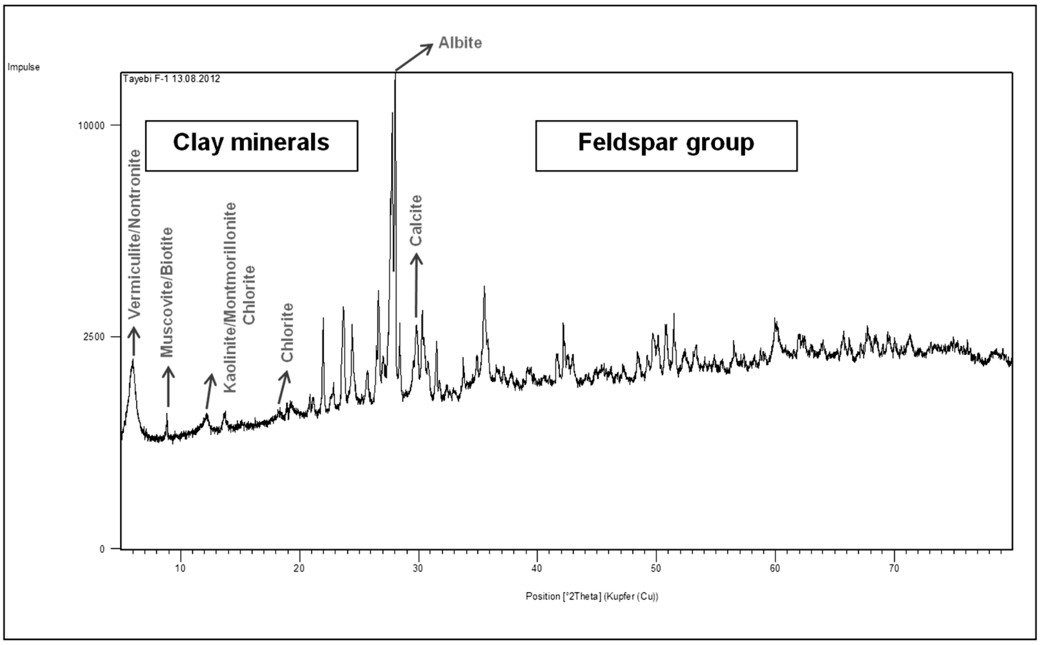
Samples were sent to XRD laboratory for the study of their minerals and their corresponding phases. The result of the XRD is shown in figure 130. Our concentration was mainly on samples from locations D, E, and F.



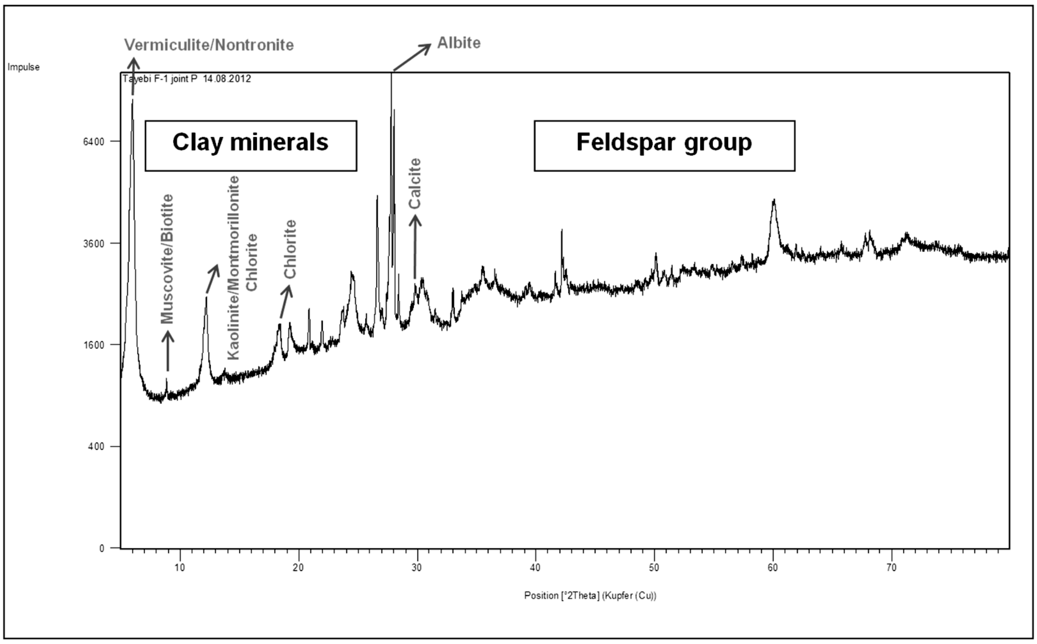
(a) Sample E (rock)



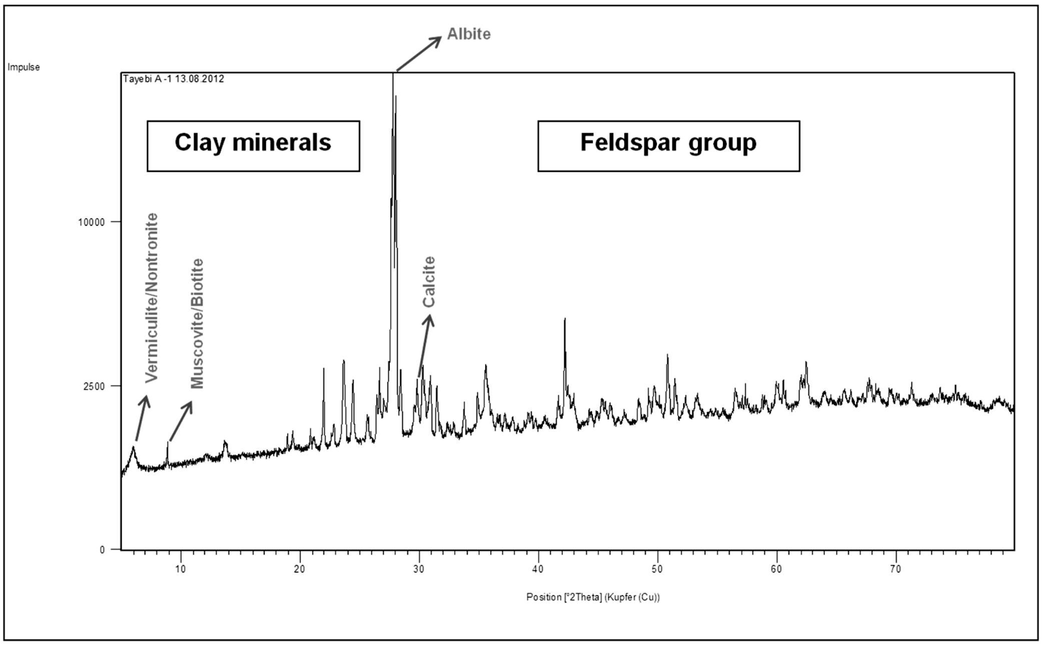
(b) Sample E (rock fillings, spacing and joints)



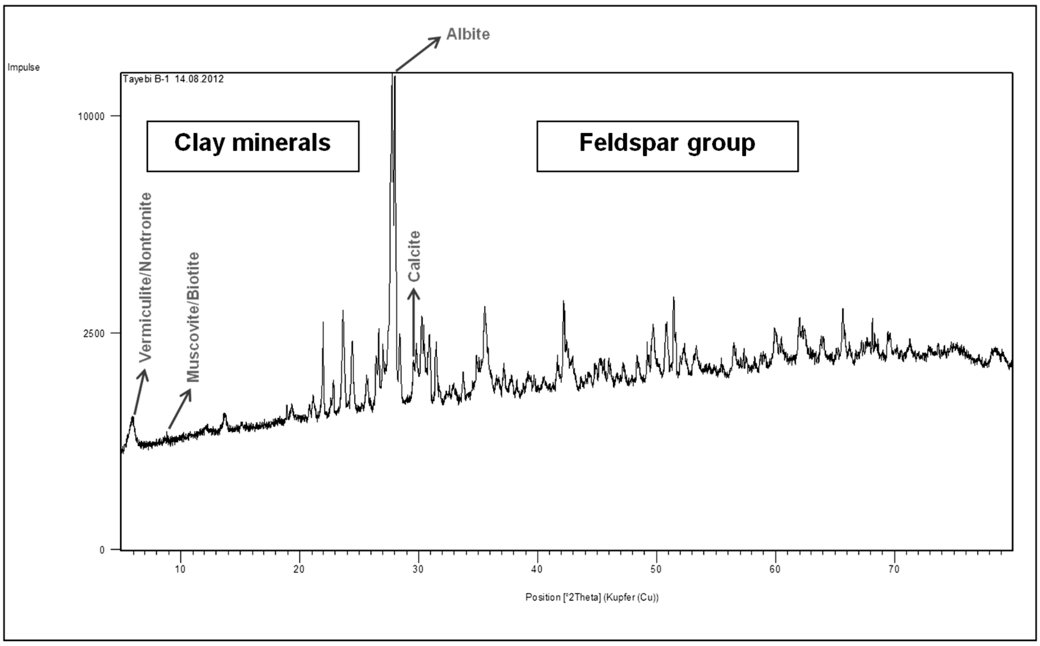
(c) Sample F (rock)



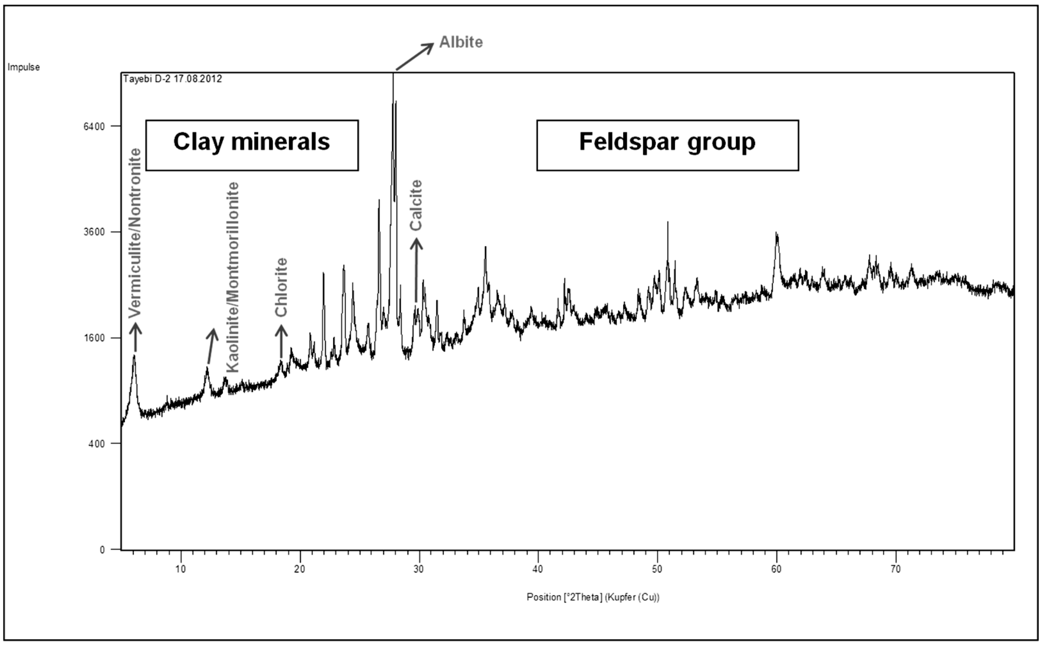
(d) Sample F (rock fillings, spacings and joints)



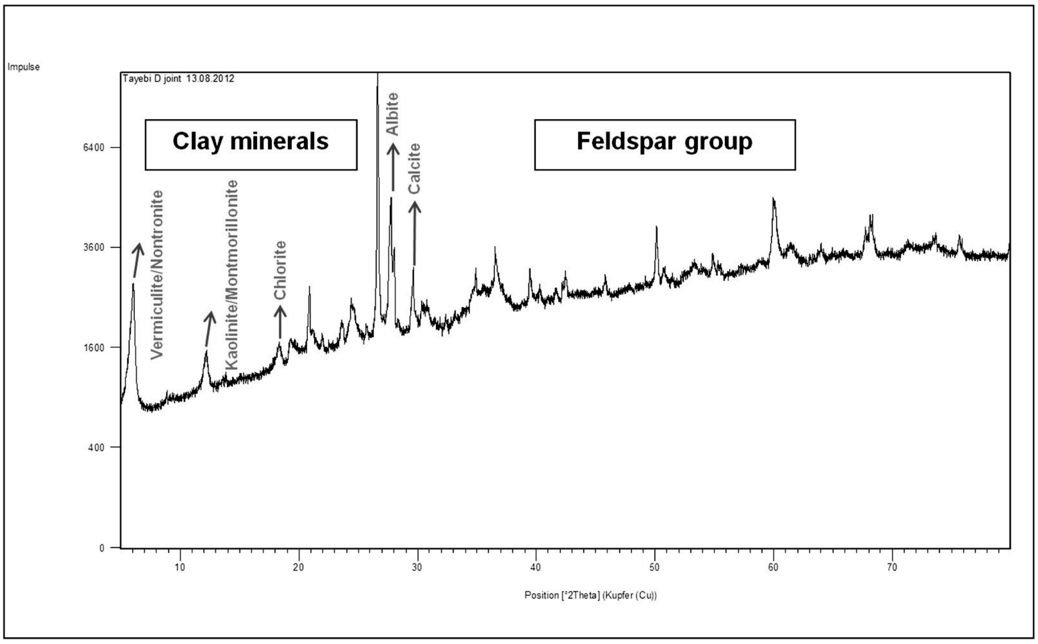
(e) Sample A (rock)



(f) Sample B (rock)



(g) Sample D (rock)



(h) Sample D (rock fillings, spacings, and joints)

Figure 130 : Results of the XRD studies on the new gathered samples

It is completely visible from the XRD results that the samples from locations D, E and F have higher contents of clay minerals in their structure than other samples like A and B. This is due to their alteration type and the advanced alteration process that occurred in samples D, E and F. Comparing the XRD results of the rock with its corresponding rock fillings/joints/spacings material, reveals this fact that spacings and joints in area D, E and F contain even more clay minerals. Thus, more undesirable and deleterious materials are in their structures. The existence of such harmful minerals (e.g., clay minerals) influences the rock durability and causes early disintegration of the rock. It will show its effect in asphalt as increase in loss of stability as well as increment in swelling percentage.

12.2.5 Natural weathering test

To be more precise and to observe the effect of real weathering on the rock samples from the new anomaly, a natural weathering test was applied (instead of simulating the weathering process by laboratory experiments such as ethylene glycol test). For the natural weathering tests, the samples gathered from the quarry (sampling locations were marked in figure 128) were exposed to outside natural weather for a long period of time and the effect of natural weather on the samples was studied. They were placed outside for more than two and a half years. However, samples from the new altered zones (D, E and F) were disintegrated in the first four months (01.10.2012-01.02.2013). It shall be noted that within these four months temperature had a fluctuation of -10°C to 18°C. As an example for this degradation and collapsing process, figure 131 is referred. It is visible from the figure, that the samples from point “E” were broken down and disintegrated to a great extent within a period of four months.

(a) Before natural weathering test (start date: 01.10.2012)

(b) Natural weathering test (after 114 days, date: 01.02.2013)

(c) Natural weathering test (after 947 days, date: 15.05.2015)

Figure 131 : Samples gathered from location E (new altered zone) before (a), after being exposed to natural weathering test for a period of four month (b) and thirty months (c)

It shall be mentioned that samples with high LOI and low MAG values were also disintegrated but with a slower rate. Samples with low LOI and high MAG values are still healthy, strong, fresh, and robust.

12.3 Phase III: Determination of thresholds

To be able to control the situation (which is very similar to the case of railway ballast) both qualitatively and quantitatively, the thresholds for MAG and LOI values of the aggregates must be determined. However, this time the threshold determination is performed in accordance with the requirements defined for asphalt applications. In other words, in order to ensure a good and acceptable quality for the produced asphalt, the determination of LOI and MAG thresholds are inevitable.
Therefore, this phase is split into three parts: sampling, MAG/LOI measurements, and final asphalt experiments.

12.3.1 Sampling

The new anomaly and its affected areas were perfectly recognized on the basis of the results obtained from last phases (I and II), and thus a new sampling stage was defined. The sampling was carried out from five locations of the quarry for the purpose of asphalt experiments. The locations were selected in a way that different groups of LOI/MAG values were covered. Figure 132 shows the locations of sampling for the planned asphalt tests. For more accuracy, sampling was performed in two manners: the first group of samples was taken by hand (as hand-pieces) from four locations (A, E, G and J) and the second group of samples was collected from the end product of the processing plant (G, J and M). This means each location was blasted separately and then the material in the muck-pile was fed to the plant (by normal mining operation) and then the crushed end-product namely the aggregates was sampled and sent to the laboratory to be used for asphalt experiments.

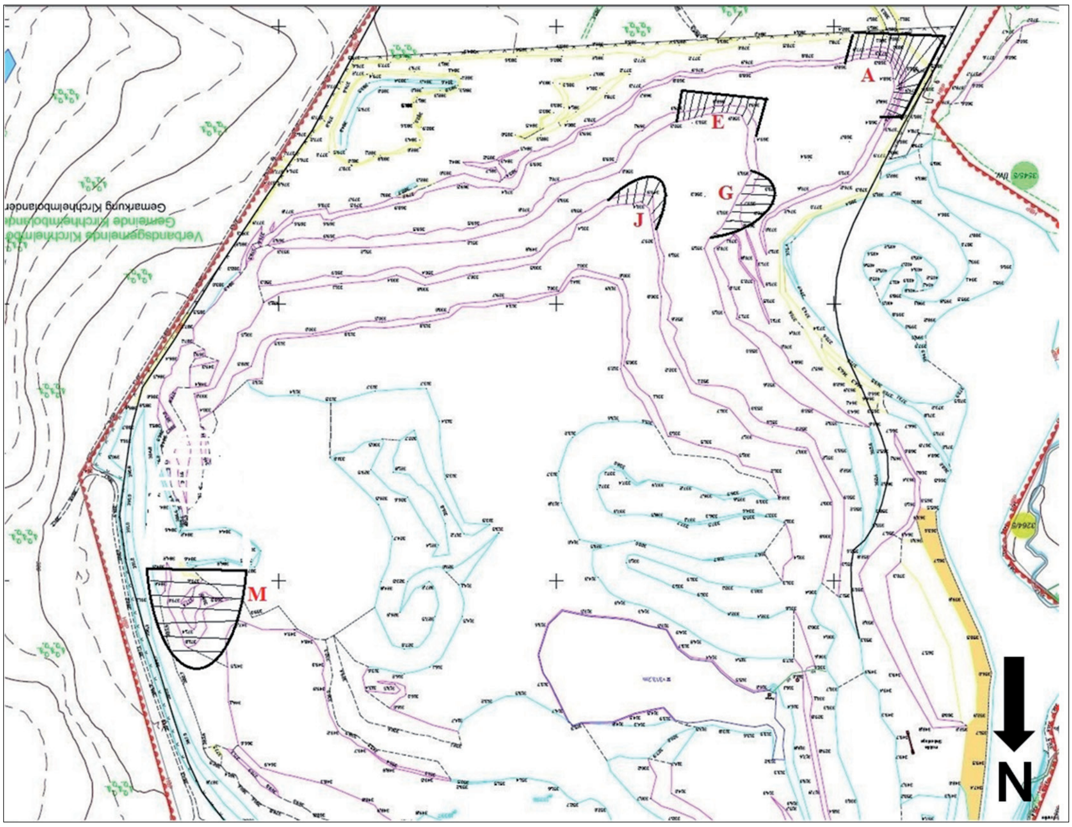


Figure 132 : Sampling locations for asphalt experiments (A, E, G, J, M)

All the gathered samples were sent to the asphalt laboratory for further asphalt tests. Nevertheless, prior to the asphalt tests they were proved for their MAG and LOI values.

12.3.2 LOI and MAG value measurements

The samples were prepared for LOI and MAG value measurements in the laboratory. The results of LOI and MAG value measurements of the samples from different locations may be seen in table 24.

Table 24 : MAG and LOI values of the samples taken for asphalt experiments

Variant	***MAG powder (x10^{-3} SI Units)***	***LOI (%)***
A (Hand)	7,398	0,548
E (Hand)	6,936	3,324
G (Hand)	4,063	1,339
G (Muckpile)	2,982	1,177
J (Hand)	5,240	0,990
J (Muckpile)	4,359	0,717
M (Muckpile)	2,041	0,946

The difference in the MAG and LOI values of the samples from the same location is due to this fact that by muck-pile sampling, the whole muck-pile is mixed and crushed thus more variety of the rocks are contained in the sample, whereas by sampling with hand the variation will be less. In other words, by hand sampling the MAG/LOI value of the rock is measured, however, in muck-pile sampling the MAG/LOI value of the rock mass is obtained.

12.3.3 Asphalt experiments and determination of thresholds

Samples from different locations of the quarry were prepared for asphalt experiments to evaluate the stability loss and swelling of the samples based on their LOI and MAG values.

12.3.3.1 Asphalt experiments

The asphalt samples were prepared (based on the recipe as before and with limestone filler) and then testes based on DIN Standard and TP-Asphalt (as mentioned before).

The swellings and stability losses of different samples were measured and plotted against their corresponding MAG and LOI values. In order to find an accurate threshold for MAG and LOI factors (as two indicators for asphalt quality assurance) at least 200 asphalt samples were produced for this phase of studies.
The experiments in this phase were divided into two groups: short-term and long-term experiments. The main aim of this division was to observe the effect of time on the stability and swelling of the samples. The detailed information regarding each group is discussed in its corresponding section respectively.

12.3.3.1.1 Short-term experiments

As mentioned before sampling was performed from five distinct locations and in two different methods. A set of sampling are named as “hand sampling” and the other set is called “muck-pile sampling.” The hand sampling was perused right in the quarry and at the desired location points and done with hand and then crushed and sieved in the laboratory, while the muck-pile sampling was actually performed from the blasted muck-pile but after the crushing and sieving process in the plant.
For this stage, the asphalt samples were produced (from all five different aggregate samples) in the asphalt laboratory in a standard manner. One day after their production, they were examined in conformity with the available standards (every single procedure such as heating, mixing, conditioning of the asphalt samples for 48 and 72 hours in water and etc. was done based on defined standards).
In order to be more precise for this part of experiments, the effect of the influencing factors namely LOI and MAG values of the samples, were assessed separately on the stability and swelling parameters. The results of different aspects are discussed below.

12.3.3.1.1.1 Effect of loss on ignition

In this stage, the effect of aggregate LOI on swelling and stability of the samples was tested. LOI is the volatile content of a material from which majority of it, is water. On the other side, a higher content of aggregate LOI also means a higher alteration degree, which is undesirable and harmful for asphalt. Therefore, the concept that a higher water content and larger extent of alteration logically may lead to a higher amount of swelling and correspondingly a larger loss in stability will be tested.

The asphalt samples from all the different groups were examined for their swelling and stability. Figure 133 shows the Marshall swelling (48 hours swelling) of different groups against the LOI values of each group.

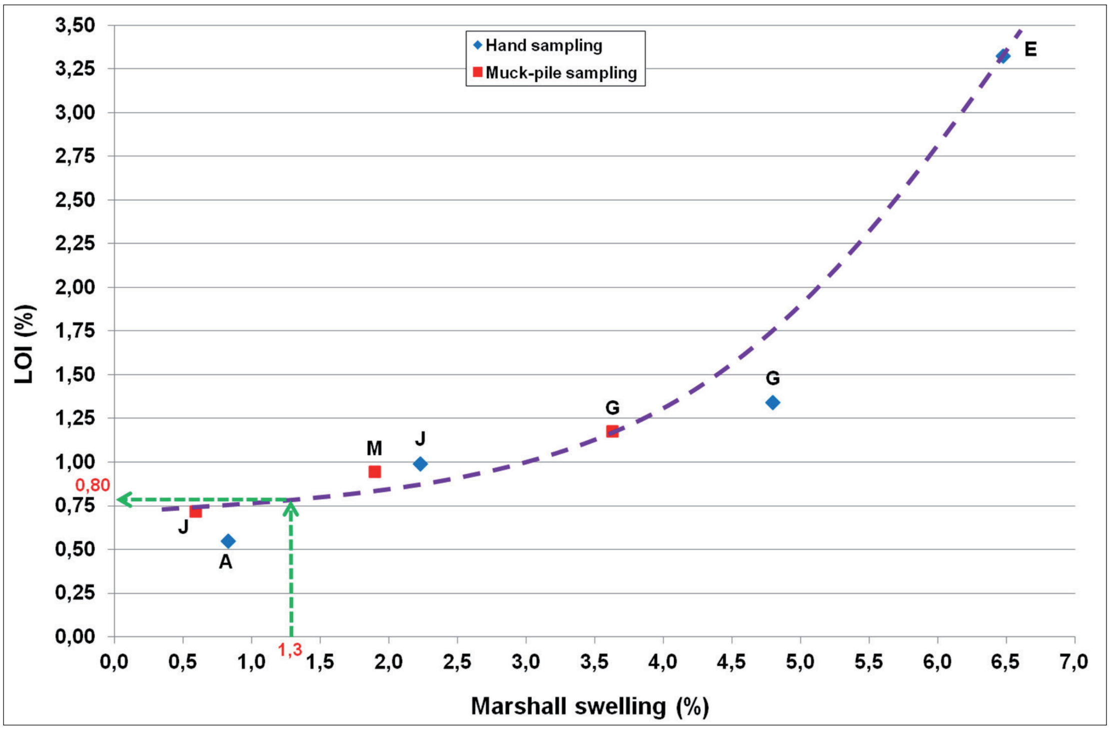


Figure 133 : Marshall swelling vs. LOI values of different asphalt groups. The threshold of LOI is about 0,80% on the basis of the regional requirements for the maximum allowed swelling percentage which is defined to be 1,3%. The value of 1,3% is determined by the regional authorities with regard to asphalt quality control conditions in each state.

The trend of the graph in figure 133 reveals the fact that with an increase in LOI value, the Marshall swelling also increases which is very logical and in accordance with all the topics which were discussed up to this point. The sample with the least LOI value has also the lowest swelling percentage and the sample with the highest LOI value has the largest swelling percentage. It is concluded from this graph that the Marshall swelling has a direct relation with the volatile content (LOI) of the aggregates, which are the major components of asphalt concrete (up to 95%).
In the next step, the effect of loss on ignition of the aggregates on the Marshall stability loss of the asphalt samples will be examined.

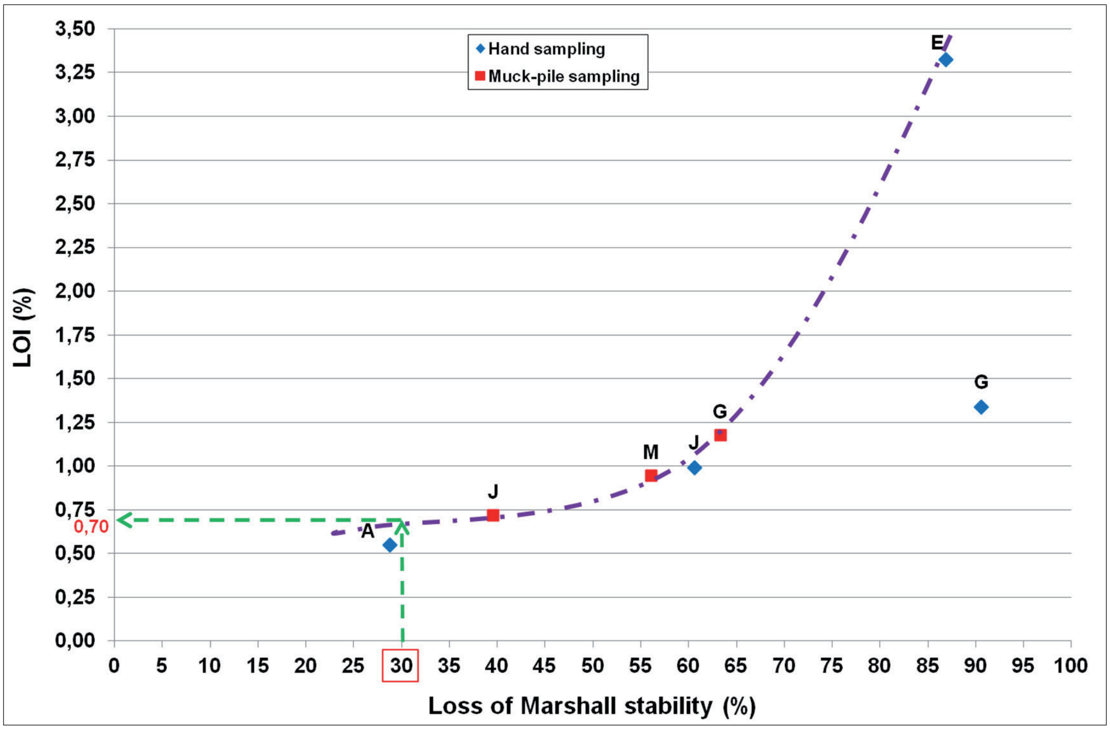


Figure 134 : Loss of Marshall stability vs. LOI values of different asphalt groups. The threshold of LOI is about 0,70% on the basis of the regional requirements for the maximum allowed Marshall stability loss which is defined to be 30%. The value of 30% is determined by the regional authorities with regard to asphalt quality control conditions in each state.

Regarding figure 134 which shows the Marshall stability loss of different groups against the LOI values, it shall be noted that the same rule is also true here, which means with increase in LOI values, the amount of loss in Marshall stability increases as well. The trend is exactly similar to the relationship between LOI and swelling. The asphalt samples with the lowest LOI have the least loss in Marshall stability and samples with the highest LOI have the highest loss of stability.

In the next figure the 72 hours swelling is illustrated as a function of LOI of the asphalt samples. The same as before, a rise in LOI value leads to an increment in 72 hours swelling value.

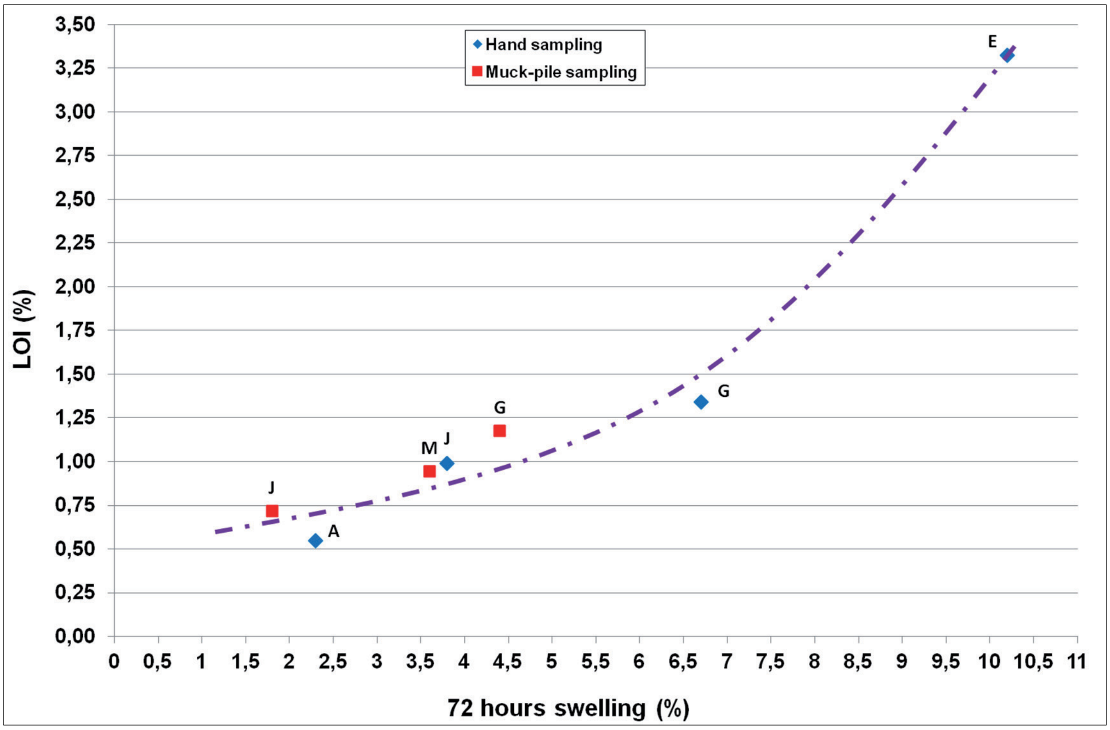


Figure 135 : 72 hours swelling vs. LOI values of the asphalt samples (the respective authorities define no proper requirements for the maximum 72 hours swelling value)

In figure 136, the relationship of LOI with Indirect Tensile Strength (ITSR) of the asphalt samples is shown.

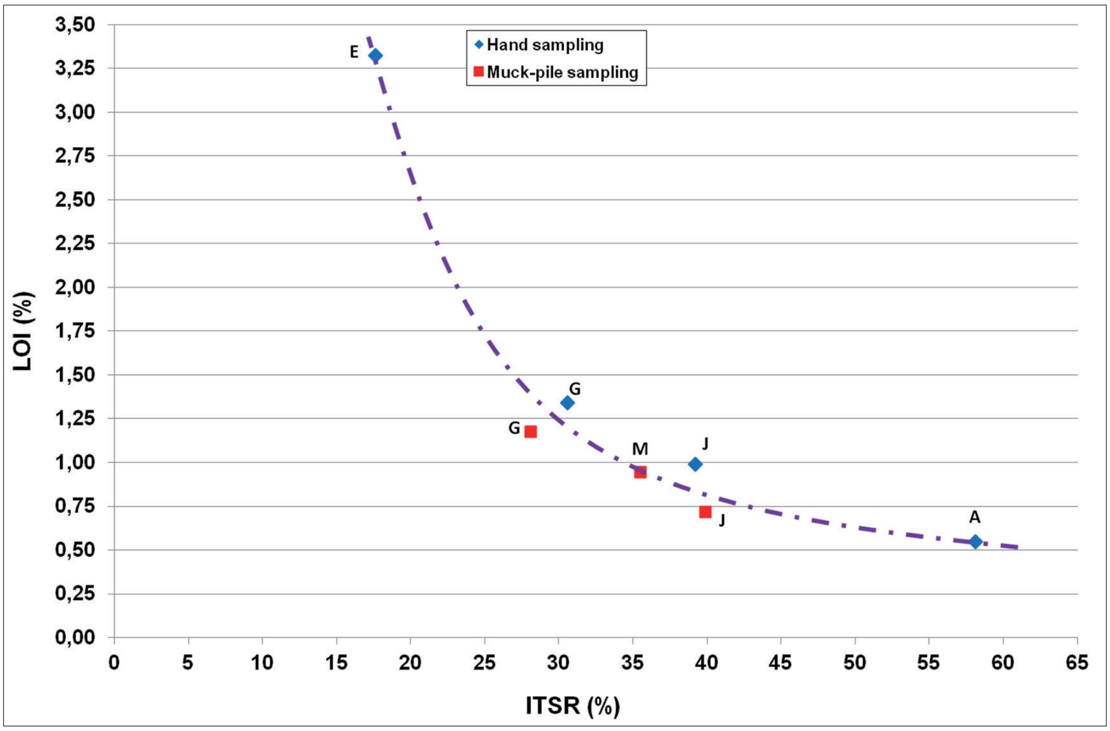


Figure 136 : Indirect Tensile Strength vs. LOI of the asphalt samples (the respective authorities have not defined any proper requirements for the maximum ITSR value)

The graph in figure 136 also complies with previous results. Since ITSR is the remaining strength of the asphalt samples after conditioning, its value increases as the LOI value decreases and vice versa. This is completely true and is actually the right outcome.

12.3.3.1.1.2 Effect of magnetic susceptibility

The effect of the magnetic susceptibility (of the aggregates) on swelling and stability of asphalt was approved in the last chapter. Here just as a confirmation of the previous outcomes, the results of asphalt stabilities and swellings of different groups are plotted against their corresponding MAG values (figure 137 and 138).

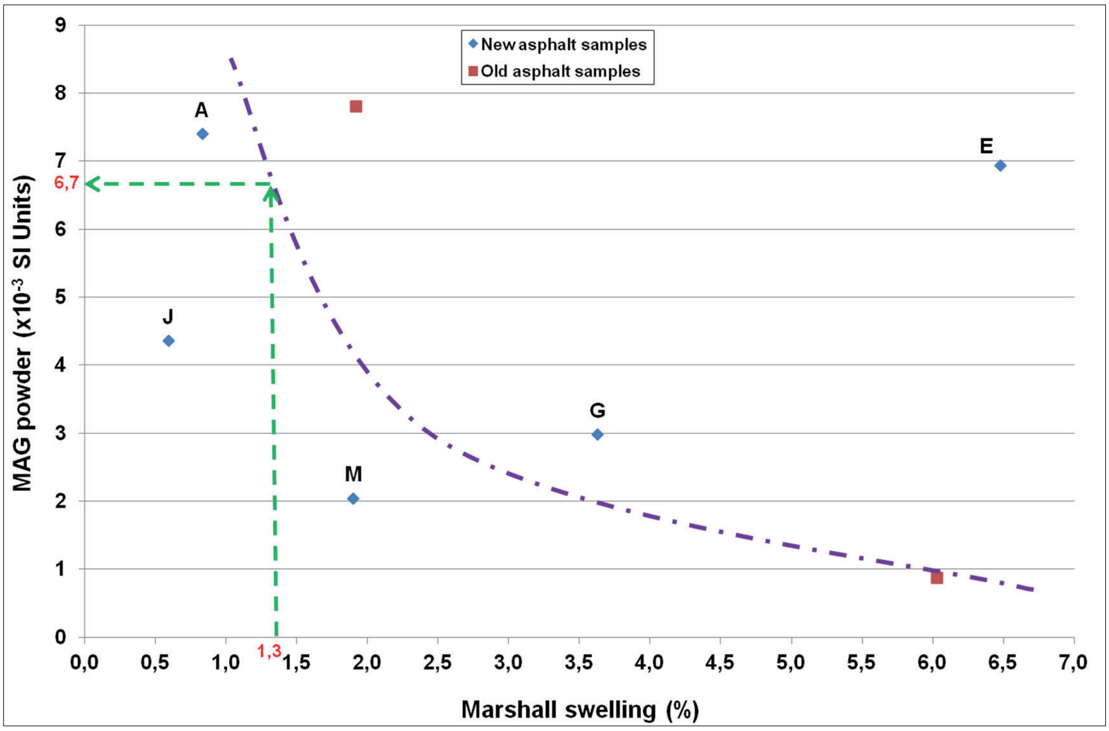


Figure 137 : Marshall swelling vs. MAG values of different asphalt groups. The threshold of MAG value is about 6,70x10^{-3} SI Units, on the basis of the regional requirements for the maximum allowed Marshall swelling which is defined to be 1,3%. The value of 1,3% is determined by the regional authorities with regard to asphalt quality control conditions in each state.

It is obvious from the graph that there is an inverse relationship between the swelling and MAG values. A rise in MAG value leads to a decrease in Marshall swelling which is completely right.

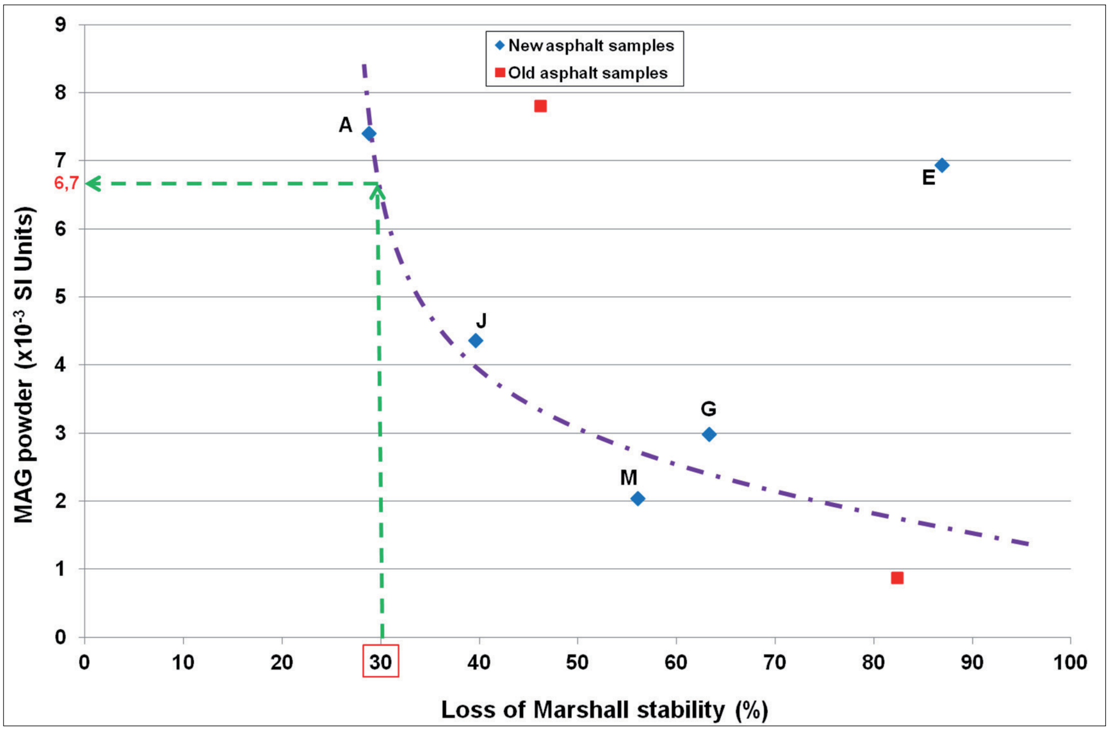


Figure 138 : Loss of Marshall stability vs. MAG values. The threshold of MAG value is about 6,70x10^{-3} SI Units, on the basis of the regional requirements for the maximum allowed loss of Marshall stability which is defined to be 30%. The value of 30% is determined by the regional authorities with regard to asphalt quality control conditions in each state.

The same relationship (as before) prevails for the MAG-loss of Marshall stability. This means the higher the MAG value the lower the loss of Marshall stability (as expected).

12.3.3.1.2 Long-term experiments

For this section of studies, after the production of asphalt samples, they were exposed to natural weather for different periods of time instead of being tested due to DIN/TP-Asphalt Standards.

The samples were exposed to natural weather for a period of one and two months. The time interval was within wintertime and the temperature fluctuation was from 8°C to -10°C.

Figures 139 and 140 show the effect of natural weathering on the Marshall swelling after one and two months. As before the direct positive correlation between LOI and Marshall swelling is valid here as well.

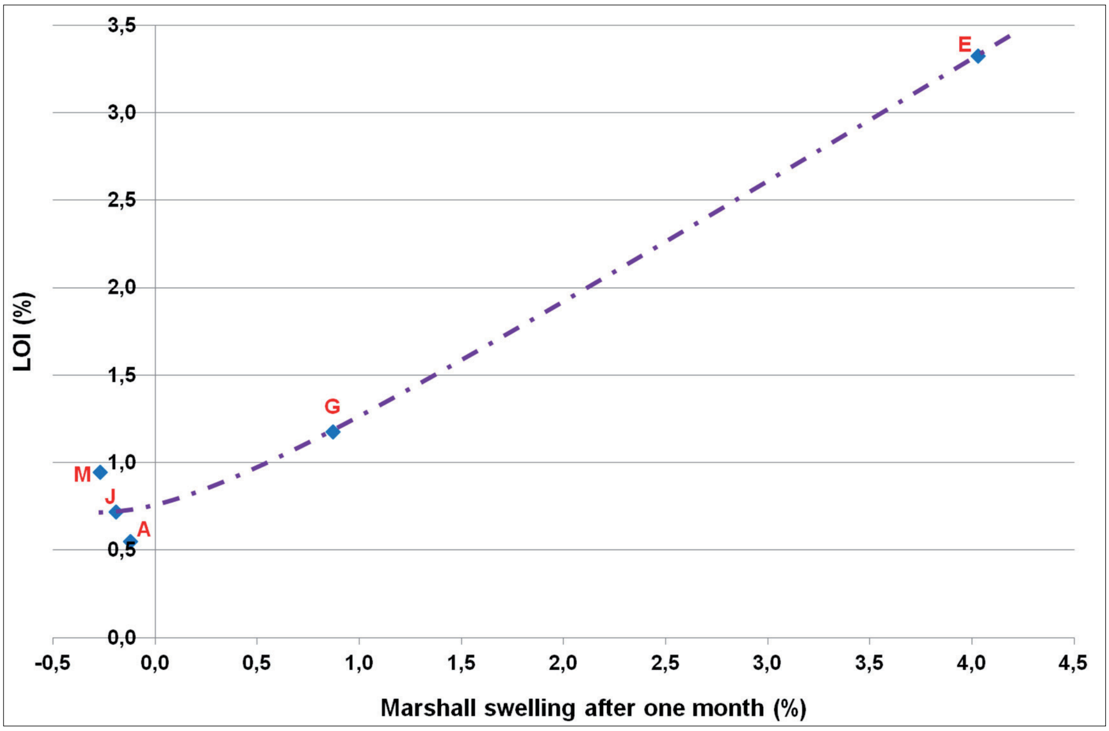


Figure 139 : LOI vs. Marshall swelling after one month under natural weather condition (temperature range: -10°C to 8°C)

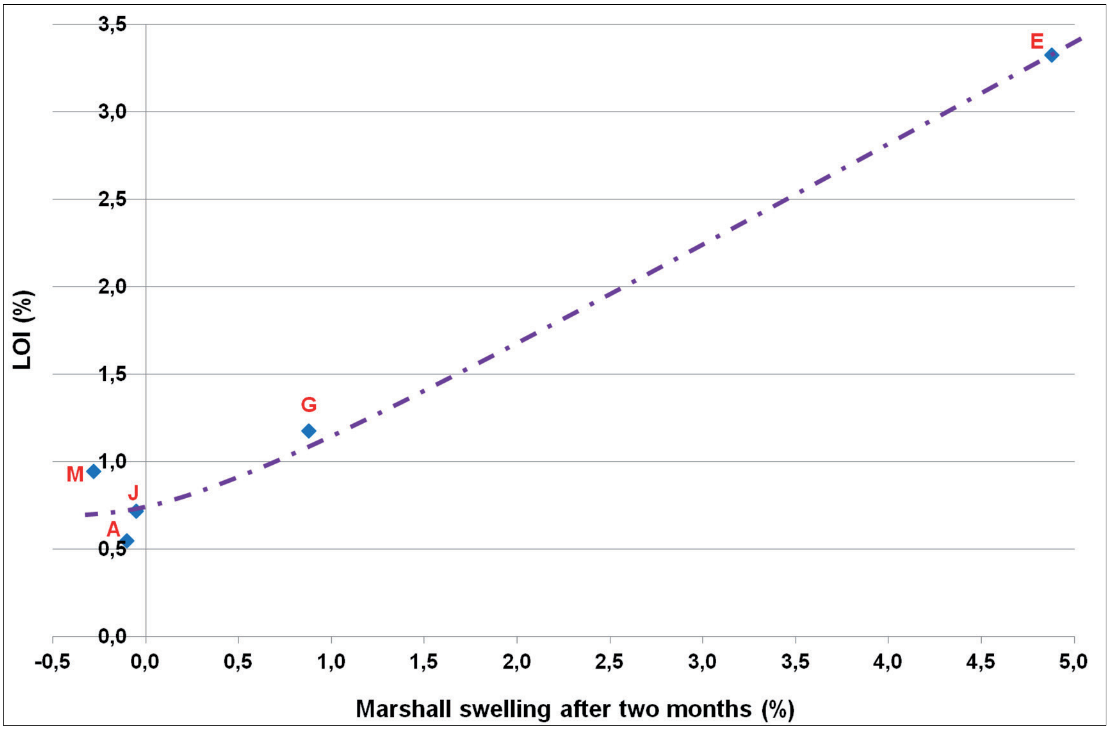


Figure 140 : LOI vs. Marshall swelling after two months under natural weather condition (temperature range: -10°C to 8°C)

In figure 141, different sample conditionings are compared with each other. As expected, the Standard DIN evaluates the samples behavior under a rougher condition. The values gained for Marshall swelling after one and two months under extreme harsh weather condition are not still comparable with the corresponding values gained by Standard DIN. The higher the LOI value of the sample, the higher the result of Marshall swelling returned by each of the three conditioning methods. The samples with higher LOI value lead to a larger Marshall swelling when tested by Standard DIN with respect to the one-month and two-months natural weathering test.

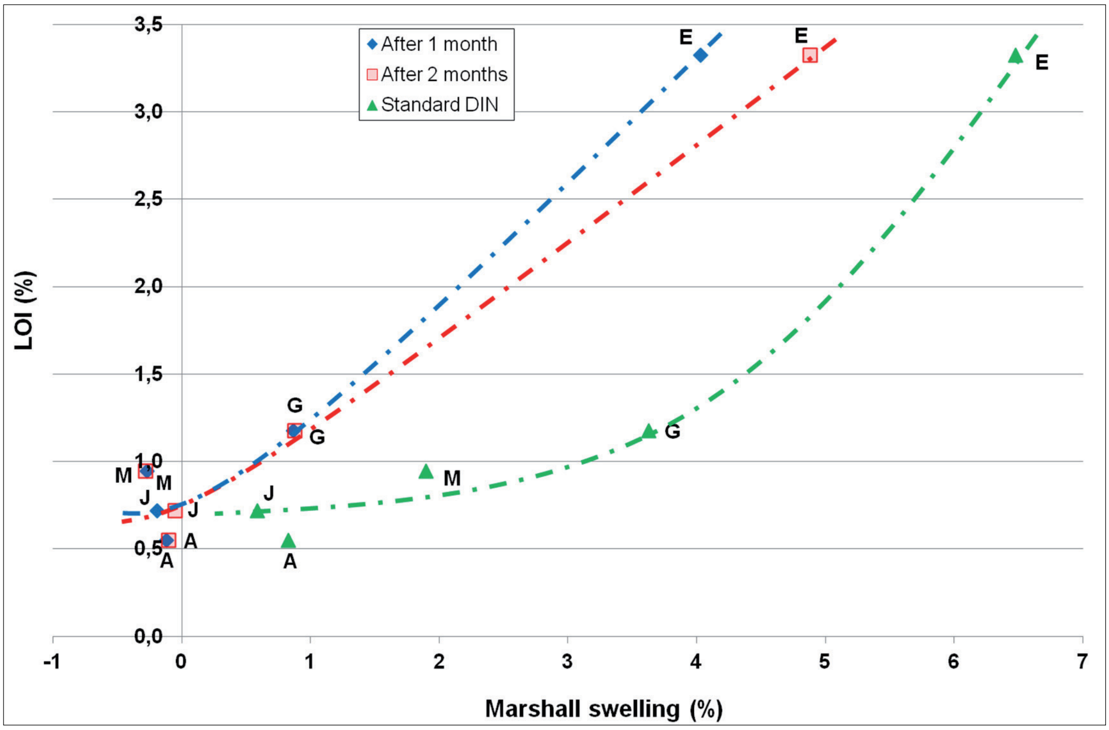


Figure 141 : LOI vs. Marshall swelling for different conditions (Standard DIN and natural weather condition)

The same sets of experiments were also applied for Marshall stability loss and the behavior of Marshall stability loss was analyzed by the passage of time under natural weathering condition. The results are illustrated in figures 142 and 143. As shown in figure 142 and 143 the loss of Marshall stability is also a function of LOI and with a rise in LOI the Marshall stability loss is also increased. This phenomenon is in accordance with the behavior of the samples with regard to Marshall swelling.

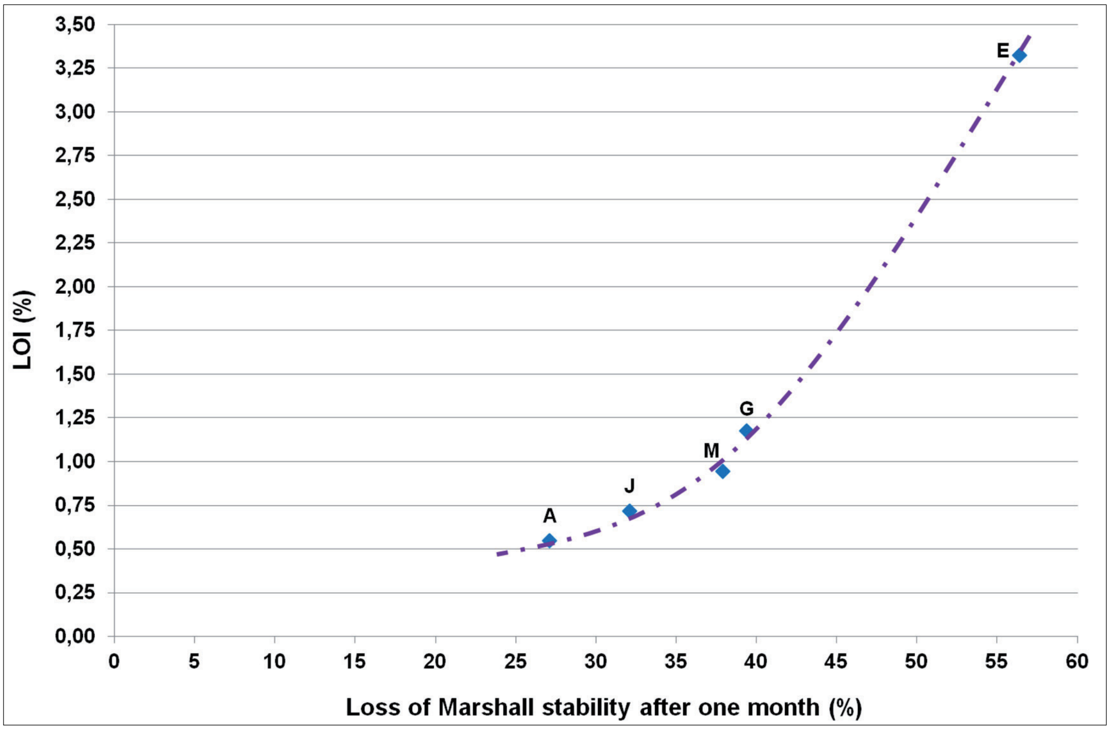


Figure 142 : LOI vs. Marshall stability loss after one month under natural weather condition (temperature range: -10°C to 8°C)

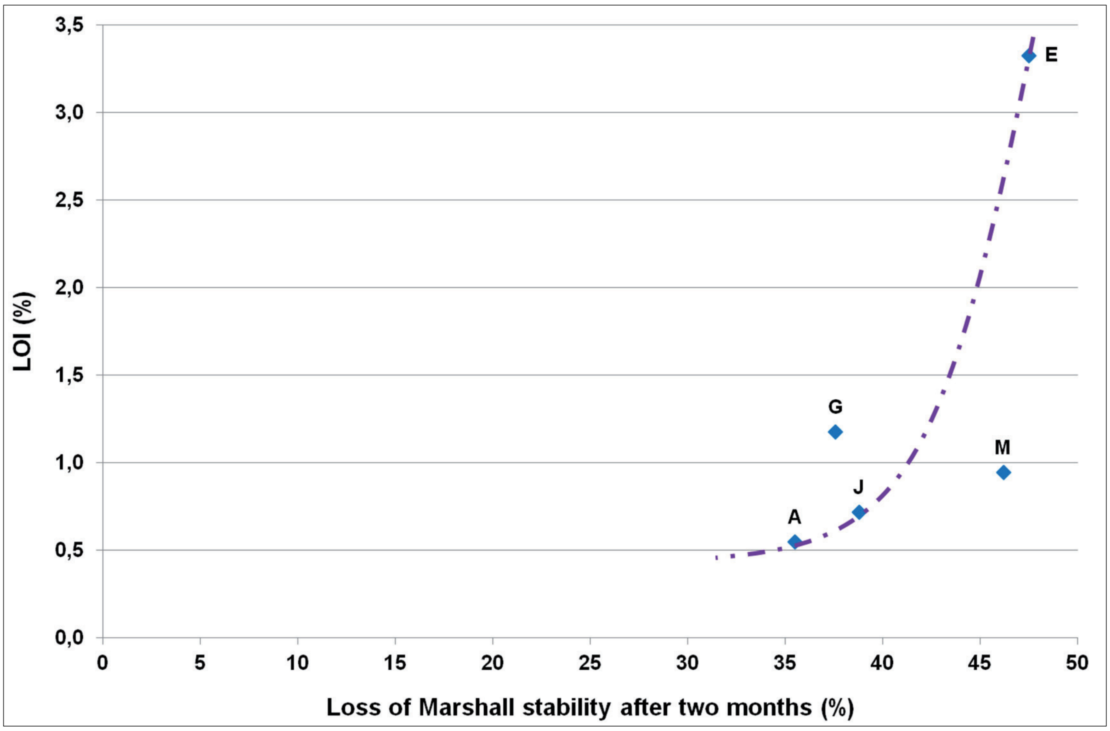


Figure 143 : LOI vs. Marshall stability loss after two months under natural weather condition (temperature range: -10°C to 8°C)

Figure 144 shows all different situations (experiments based on Standard DIN, one month natural weathering and two months natural weathering) in one graph. Similar to figure 141, in this case the Standard DIN method returns the highest values for loss of Marshall stability. This is the result of the hard and severe situations that the samples go through when they are tested based on Standard DIN. The samples with higher LOI value lead to a larger stability loss when tested by Standard DIN with respect to the one-month and two-months natural weathering test.

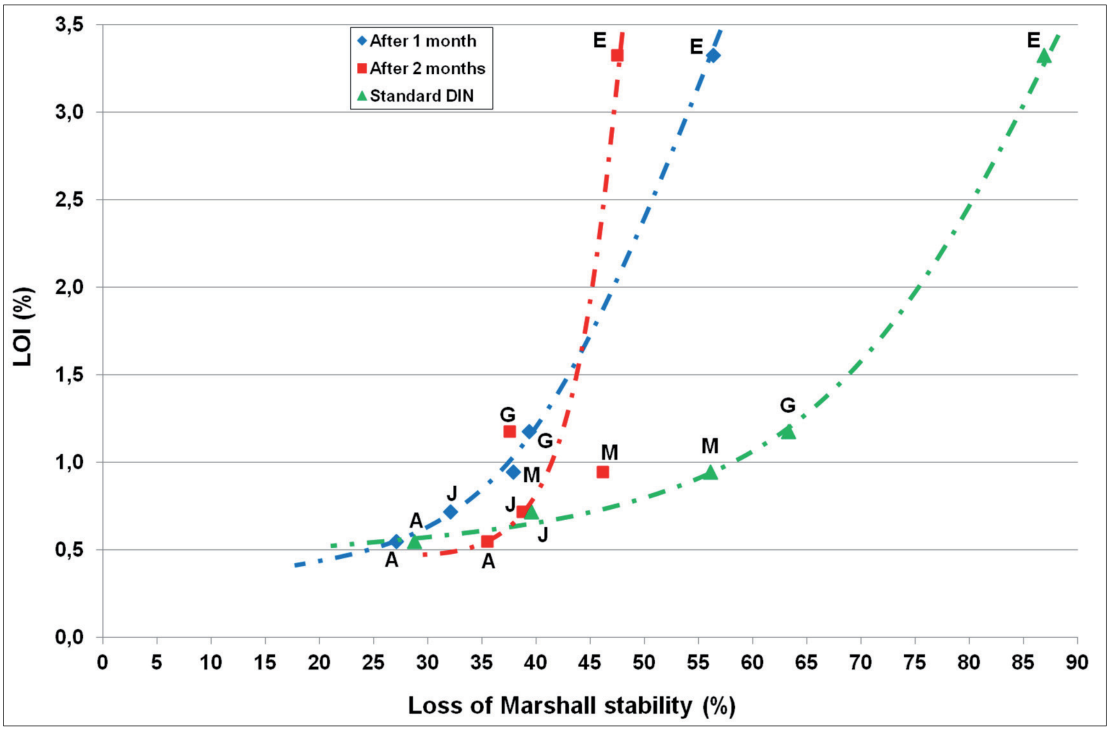


Figure 144 : LOI vs. Marshall stability loss for different conditions (Standard DIN and natural weather condition)

12.3.3.2 Determination of thresholds

Based on the studies made on the quality of the aggregates, it was observed that fixing a MAG value threshold of $4{,}70 \times 10^{-3}$ SI Units on the drill cuttings in the mining site, minimizes the effect of alteration, thus leads to the selection of high quality aggregates. This threshold was applied on the aggregates for railway ballast applications as well as asphalt usages. However, after the mining operation was confronted with the new anomaly, which had a high MAG value as well as high LOI value, it was decided to integrate the LOI value (as the second quality criterion) into consideration in order to minimize the risks. On this basis, additional asphalt tests were done and according to the results of swellings as well as the stability losses, a new threshold for asphalt operations (but this time for both quality factors) was defined.

The asphalt produced by the HMA production plant has to meet some specific requirements. The regional authorities define these obligations. In this case, our industry partner had to obey the requirements described in the “Landesbetrieb Mobilität Rheinland-Pfalz 2007-2008” [202]. According to the LBM Rheinland-Pfalz, the swelling and Marshall stability loss has to follow the determined thresholds defined by this authority. The limit for Marshall swelling of asphalt samples must be less than 1,30% and the Marshall stability loss has to be less than 30% (a loss less than 30% is desired meaning that the asphalt sample has to have a stability remainder of at least 70%). Due to this obligation, the new thresholds for MAG value as well as LOI value were defined, based on the complementary asphalt experiments mentioned in this chapter. Referring to figure 133 and assuming a Marshall swelling limit of 1,30%, a value of 0,80% is returned for LOI. By applying the same method on figure 134, but this time adopting the 30% Marshall stability loss, a LOI value of 0,70% is generated. This shows that with respect to Marshall swelling the threshold for LOI will be 0,80% and on the other hand with regard to Marshall stability loss the limit for LOI will be 0,70%. As a result to select a good trustable threshold for the LOI value, 0,75% is chosen. Therefore, the limit for loss on ignition of the aggregates used in asphalt mixture is set to 0,75%.

For defining a limit value for magnetic susceptibility of the aggregates used in asphalt production, figures 137 and 138 are referred. In both cases whether the threshold of Marshall swelling is used or the limit for loss of Marshall stability is applied, the returned MAG value is equal to 6,70x10^{-3} SI Units.

As mentioned before, prior to encountering the new anomaly, the high quality aggregates (for ballast applications) were defined as the aggregates having a MAG value greater than 4,70x10^{-3} SI Units and the LOI value was not meant to be measured. However now apart from the MAG threshold, a LOI threshold is also defined. On the basis of additional asphalt experiments, the thresholds for LOI and MAG value are determined to be 0,75% and 6,70x10^{-3} SI Units respectively (for asphalt applications). Considering this fact that the high amount of MAG limit value is resulted only from the existence of the new anomaly, which had a high MAG value, and this anomaly can also be recognized through its extremely high LOI value, therefore the old threshold for MAG value is still valid. In other words if there were no LOI measurements, then for 100% certainty the MAG limit value could have been expected to be around $6,70x10^{-3}$ SI Units. However, since it is suggested to measure both factors as the quality control parameters, assuming LOI threshold 0,75% and MAG threshold $4,70x10^{-3}$ SI Units, will satisfy the asphalt quality.

Based on the experiments carried out in this chapter and the discussions, the thresholds for LOI and MAG value are determined. The limit value for LOI is 0,75% on powder with grain size smaller than 1 mm and the threshold for MAG value is $4,70x10^{-3}$ SI Units on the drilling fines. As a general rule to be implemented by the mining staff or the staff of the asphalt plant, in order to be able to guaranty a continuous high quality asphalt products, the below mentioned suggestions must be taken to account:

i. The MAG value (of the drill cuttings) has to be measured at first. If the MAG value is smaller than the threshold value ($4,70x10^{-3}$ SI Units) then the measurement of LOI is not needed. The quality of materials is known as poor and may not be used for asphalt production purposes.
ii. If the MAG value is larger than the threshold ($4,70x10^{-3}$ SI Units) then to eliminate the risks and to enhance the confidence, the LOI value must be measured. If the LOI value is under its threshold which is 0,75% then the quality of the materials is regarded as high and can be used for asphalt production, otherwise if the LOI value is higher than 0,75% then the quality of the materials is evaluated as poor and the materials must not be used for the purpose of asphalt production.

12.4 Results and discussion

The existence of a new anomaly in the quarry was approved via different types of investigations. In this kind of anomaly, because of its special form of hydrothermal alteration, the magnetite content of the rock either remains the same or increases. Therefore, the altered rock will expose a high magnetic susceptibility value as well as a high loss on ignition value of itself. To overcome this problem and to guaranty the usage of good quality aggregates for asphalt applications, different types of asphalt experiments were carried out. On the basis of the regional requirements for asphalt swelling and stability loss of asphalt samples, the new thresholds for MAG value as well as LOI value were defined. The limit determined for MAG value is as before $4,70x10^{-3}$ SI Units and for LOI is 0,75%. The MAG value is measured on the drill cuttings at the mining site and the LOI value is assessed on the powders with grain size less than 1mm with the use of a muffle furnace.

As a result of our complimentary studies, in order to assess the quality of the aggregates for asphalt production objectives, at the first step the MAG value has to be measured. If the MAG value of the cuttings is less than the threshold value ($4,70x10^{-3}$ SI Units), then the quality of the aggregates is low and the LOI measurements is not foreseen. In case the MAG values are larger than the threshold value, to omit the risks, the LOI values must be measured. If the LOI value is less than the LOI threshold (0,75%) then the material is a good quality aggregate and if the LOI value is larger than the limit, then the aggregate is regarded as a poor quality material and must not be used for asphalt production purposes.

13 The feasibility of transferring the results on a second quarry

To evaluate the quality of natural crushed rocks in civil applications with concentration on railway ballast and asphalt industry, two different criteria were developed as a result of investigations and researches carried out due to this research project. These two factors namely loss on ignition and magnetic susceptibility were recognized as “quality indices.” They revealed perfect results regarding the quality control aspects of the desired products. With the application of these two parameters the durability or correspondingly the quality of the railway ballasts as well as asphalt are estimated to a large extent. On the basis of thousands of experiments and measurements carried out for each application (railway ballast and asphalt) and for each parameter (MAG and LOI), the corresponding thresholds were defined. These thresholds are unique for each quarry.

In this chapter, the main aim is to check and control the transferability of the techniques and methods to another quarry. In other word, the target is to observe whether these two quality indices are also applicable as quality control factors to another igneous hard rock quarry.

Of course, to assess the transferability, all the steps that were applied to the first quarry were also exercised on the second quarry. However, to make it short and brief only the main aspects and results are going to be mentioned here in this chapter. The discussion on the second quarry will be divided into two parts: railway ballast and asphalt.

13.1 Railway ballast

To check the validity of the quality indices on the railway ballast, different stages such as sampling, preparation, and investigation were carried out in various phases. The geological studies showed that the rock type is andesite/trachy-andesite. With the use of thin/polished sections, the mineral phases and alteration situations were studied. The existence of alteration was approved by microscopic studies. According to geological and microscopic studies, the hydrothermal alteration of the samples had caused the replacement of magnetite mineral by limonite and hematite (in altered samples). On the other hand, the multi-elemental analysis of the samples showed that the altered samples had a higher value of LOI and potassium oxide but lower amount of sodium oxide with respect to fresh samples. The average percentage of silica content of the samples fell between 54-61 percent revealing this fact that the rock is an intermediate igneous rock (by composition type).

Based on the primary studies, the loss on ignition and magnetic susceptibility has the potential to reflect not only the alteration degree but also the quality of the desired rocks. On this basis, LOI and MAG values of the samples from the second quarry were measured. The inverse relationship between LOI and MAG values of the samples held true here as well. The altered rocks had a high LOI value but a low MAG value and the fresh rocks had a high MAG value and low LOI value.

This effect was again approved through a vast number of rock sampling operations. The samples were prepared and measured for their LOI and MAG values. To estimate the threshold values for LOI as well as for MAG, the “fractal analysis” method was applied. The probability graph of the samples can be seen in figures 145 and 146.

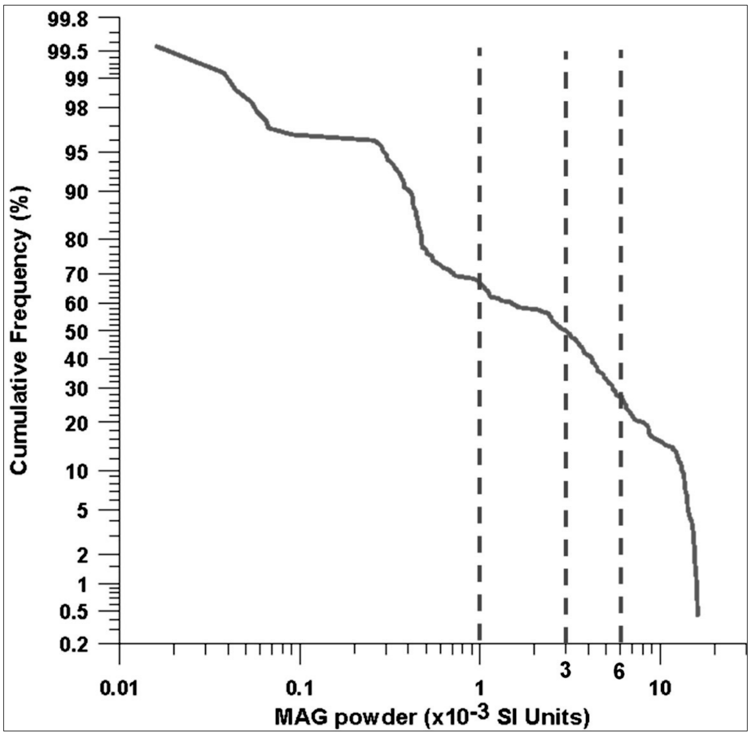


Figure 145 : Probability graph of MAG values measured on 225 powder samples

As discussed before, the inflection point(s) on a probability graph shows the separation limit(s) of different populations. Concentrating on the probability graph in figure 145 reveals the fact that there are three major inflection points at MAG values of: 1, 3 and 6 (x10^{-3} SI Units). Therefore, the MAG values of the second quarry can be divided to four distinct categories or populations as follows:

- ✓ MAG value < 1,00x10^{-3} SI Units
- ✓ 1,00x10^{-3} SI Units < MAG value < 3,00x10^{-3} SI Units
- ✓ 3,00x10^{-3} SI Units < MAG value < 6,00x10^{-3} SI Units
- ✓ MAG value > 6,00x10^{-3} SI Units

Of course there is also an inflection point on MAG value = 0,100 (x10^{-3} SI Units), but since the rock samples which had a MAG value around 0,100 (x10^{-3} SI Units) were clearly altered and tended to break down in a short time, this category is disregarded.

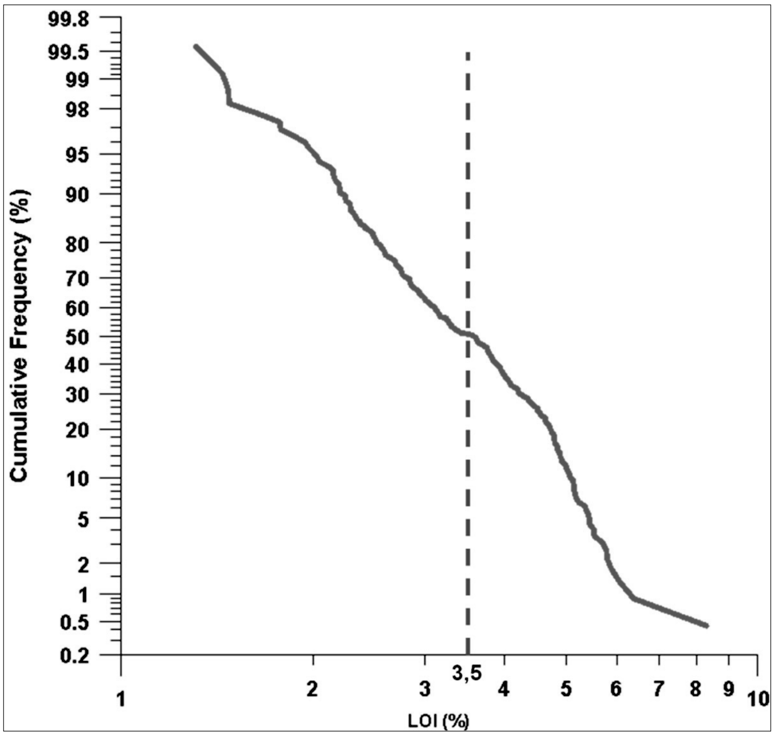


Figure 146 : Probability graph of LOI values measured on 225 powder samples

The LOI probability graph in figure 146 also shows a clear inflection point of nearly LOI=3,5%. Based on this matter, the measured LOI population has a bi-modal distribution. The total population is divided into two distinct groups, a group with LOI lower than 3,5% and a group with LOI value higher than 3,5%. The samples having a LOI value smaller than 3,5% are categorized as good quality samples and those higher than 3,5% are low quality samples.

As a result of the above estimated thresholds, since the MAG value had categorized the rock quality in a more detailed and precise way, the magnetic susceptibility of the samples was chosen as the main quality index. To validate the threshold of MAG index another stage of rock sampling was performed. In this stage, a huge number of samples were gathered in order to be able to follow the MAG grouping in a satisfactory manner. To assess the threshold predicted by MAG parameter, different types of the so-called "sound-tests" were applied to the new samples. As mentioned before the sound tests imitate the freeze/thaw cycles in the nature and for these experiments various types of solutions such as magnesium sulfate, sodium chloride and purified water (distilled water) were used in order to validate the estimated different quality-groups defined by MAG value measurements.

It is notable to mention that in this phase "glycol test" as well as "methylene blue dye test" were also applied to the samples. However, the samples did not react with glycol at all (leading to no precise and accurate results), and the results of methylene blue tests did not correspond to the reality at all. For example, there were samples that were clearly altered/weathered and were about to be disintegrated but the methylene blue test did not show any negative results meaning complete soundness of the samples (but the reality was exactly the opposite). This is due to the fact that the methylene blue dye test shows the existence of some special clay minerals mainly smectite, and if the sample does not contain these particular clay minerals, the result of this test will be positive meaning that the rock is completely perfect and has a high quality. Because of this, neither the results of glycol tests nor methylene blue test were considered. The two tests were not capable of validating the MAG threshold and therefore were neglected.

The various sound tests that were carried out on the prepared samples and their corresponding results are shown in tables 25 to 27.

Table 25 : Magnesium sulfate dye test of samples with different MAG values (threshold=3%)

	Magnetic susceptibility ($x10^{-3}$ SI Units)			
	<1	1 - 3	3 - 6	>6
Passage (%)	14,9	0,45	0,42	0,56

Table 26 : Sodium chloride dye test of samples with different MAG values (threshold=8% with 10 cycles)

		Magnetic susceptibility (x10^{-3} SI Units)			
		<1	1 to 3	3 to 6	>6
Passage (%)	10 CY	9,33	2,07	1,27	0,61
	20 CY	19,8	4,51	2,98	1,08
	30 CY	27,86	6,72	5,25	1,47

Table 27 : Distilled water dye test of samples with different MAG values (threshold=1% with 10 cycles)

		Magnetic susceptibility (x10^{-3} SI Units)			
		<1	1 to 3	3 to 6	>6
Passage (%)	10 CY	0,44	0,37	0,19	0,17
	20 CY	0,73	0,50	0,27	0,25
	30 CY	1,39	0,53	0,39	0,26

As shown in the above tables, the samples were subjected to different sound-tests and the results of sound-tests confirmed the grouping of the samples based on their MAG values. The thresholds for various solutions used in the experiments are also mentioned in each case. These thresholds are defined in the "TL-Gestein" [203] and "Bahn-Norm DBS 918061" [204]. For example, the threshold for magnesium sulfate dye test is 3%, for sodium chloride with 10 cycles is 8% and for distilled water with 10 cycles is 1%. Analyzing the results makes this point clear that samples having a MAG value less than 1,00x10^{-3} SI Units, illustrate low quality and less durability from themselves when exposed to various types of freeze-thaw tests. Interestingly as the MAG value increases, the passage percentage decreases (within each cycle), which shows an improvement in the quality of the samples. Based on the standards and requirements, the experiments shall be done with 10 cycles. However, for the purpose of our studies, in order to be more accurate and get more reliable results, experiments have been carried out up to 30 cycles. When the MAG value is greater than 1,00x10^{-3} SI Units, even with 30 cycles, the specified threshold is not reached in any type of the sound tests above.

In line with the above experiments, about 150 hand-piece rock samples were collected from the quarry and were exposed to natural weather for natural weathering test. The samples were outside for a period of one year (September 2012 to September 2013) and then were analyzed for their behavior against the weathering and alteration process. The temperature fluctuation within this period of time was 40°C (from -11°C to 29°C). Based on the observations, only the samples which had a MAG value lower than $1{,}00x10^{-3}$ SI Units were disintegrated and broken down. These samples had also a loss on ignition value of greater than 3%, which corresponds largely to the pre-defined threshold for LOI value.

Before transferring the results on the drilling fines, a vast MAG value measurement was carried out on the wall of the benches (quarry slopes). More than 3100 MAG measurements (with their corresponding co-ordinates) were applied on the walls and then the gathered data was assessed again for approving the defined threshold one more time. The fractal method was applied to estimate the threshold of the MAG value. The probability graph of the measured MAG values on the wall of the quarry benches can be seen in figure 147. According to this figure, the inflection point and thus the main threshold for the MAG value is $1{,}00x10^{-3}$ SI Units which means the limit of MAG value (as defined before) lies on $1{,}00x10^{-3}$ SI units. This result corresponds perfectly with the previous threshold of MAG value.

According to the numerous experiments performed for determining the MAG threshold value of the quarry, the value of $1{,}00x10^{-3}$ SI Units was accepted as the threshold for magnetic susceptibility factor of the powder samples from the quarry. Therefore, samples illustrating a MAG value greater than the mentioned threshold will have a good quality and samples with less MAG value, will be recognized as poor quality rocks. The transferability of this value on quarry drill cuttings and rocks was also studied in the same manner as discussed in detail in the previous chapters of this research work.

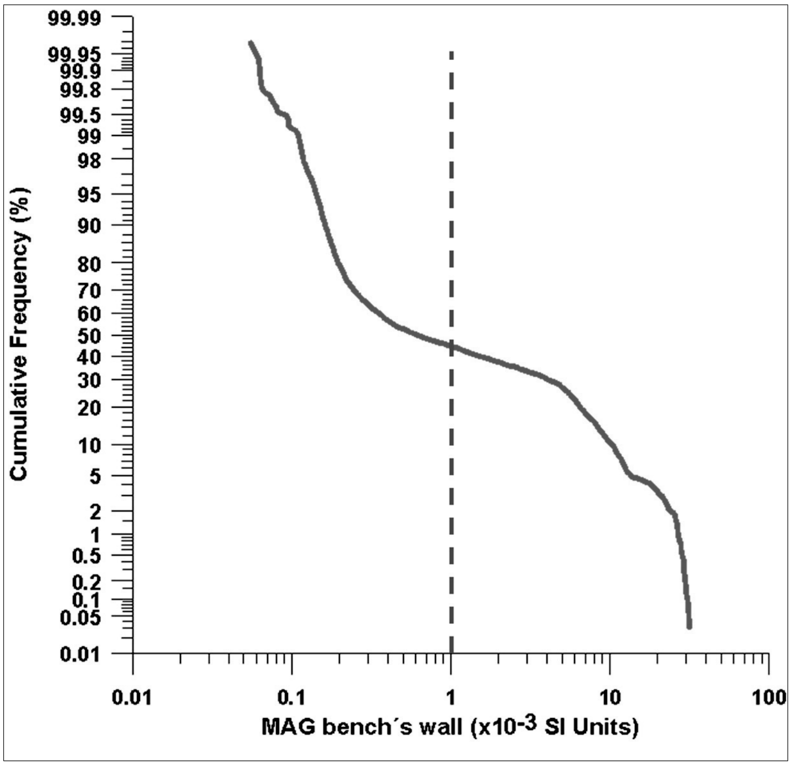


Figure 147 : Probability graph of the MAG values of the quarry slopes (3100 measurements)

MAG threshold value of the powder samples (samples with grain size less than 1mm) was transferred with complete success on the drill cuttings of the boreholes and on the quarry slopes. The correlation graph between MAG of powder samples and MAG of drill cuttings as well as MAG of powder samples and MAG of rocks is illustrated in figures 148 and 149. The regression value for both cases is very high and this means a great correlation exists between the MAG values of different states of the samples.

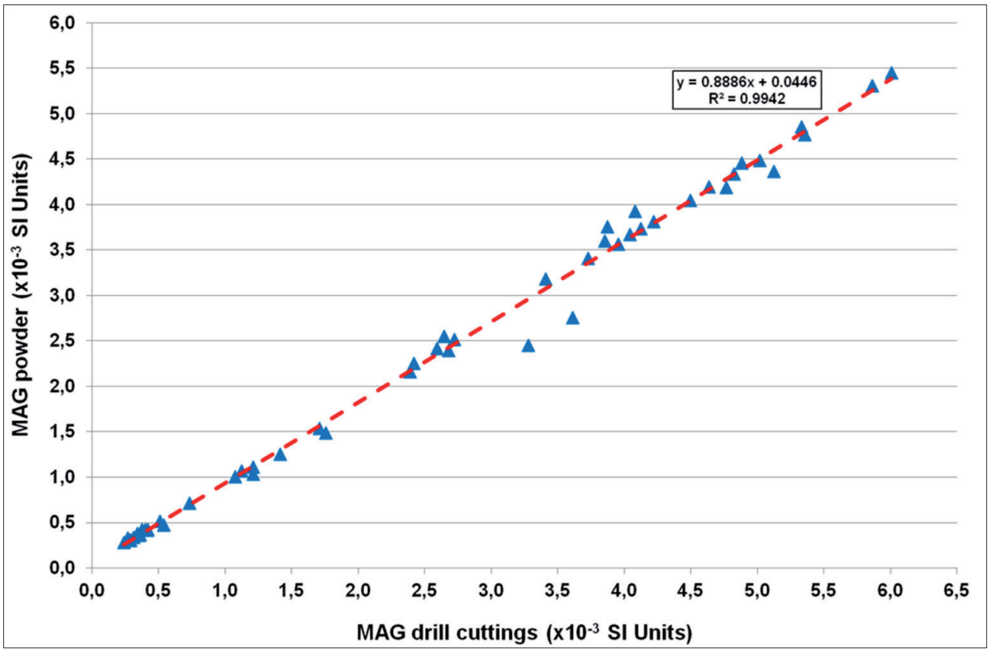


Figure 148 : Correlation graph between MAG values of powders (grain size<1mm) and drill cuttings of the boreholes

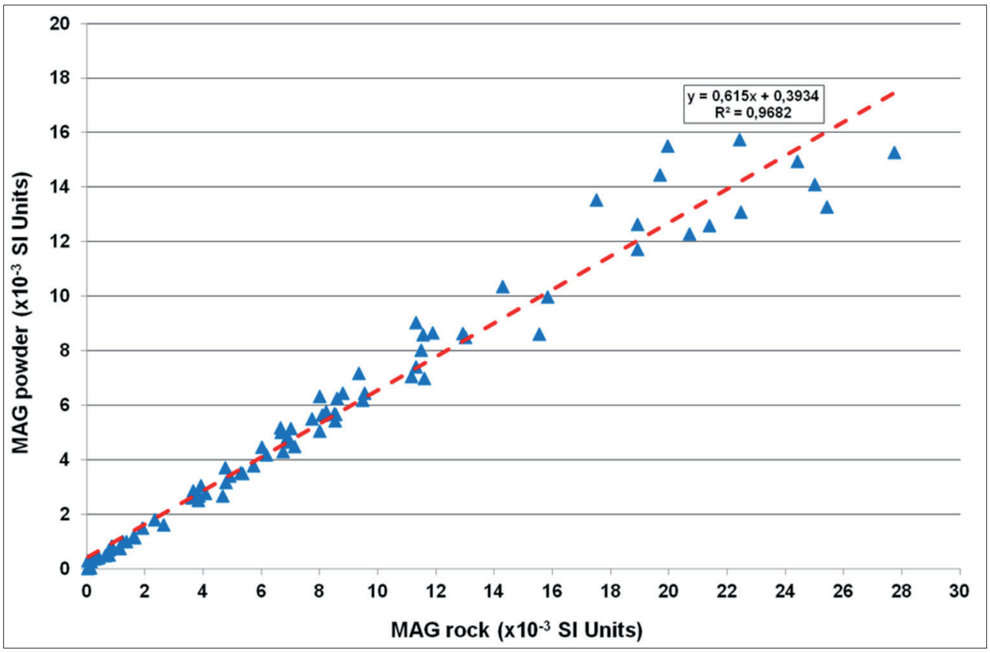


Figure 149 : Correlation graph between MAG values of powders (grain size<1mm) and rocks

With above figures, the threshold of 1,00x10^{-3} SI Units on powder samples is equal to the same MAG threshold value for rocks and drilling fines. Therefore, a universal threshold was determined for the magnetic susceptibility of the quarry and that was 1,00x10^{-3} SI Units and there is no difference if it is the MAG value of powder, drill cuttings or rock.

According to the determination of MAG threshold value, samples with MAG values greater than the defined threshold will expose a high quality behavior and samples with lower values will show poor quality of themselves.

In the next stage, a short study will be performed on assessing the MAG threshold value of aggregates used in asphalt samples.

13.2 Asphalt

To evaluate the threshold of magnetic susceptibility for asphalt applications, sampling was performed based on the MAG values and asphalt samples were produced from each group of samples. Grouping of samples was done on the basis of MAG values as mentioned in section 13.1 (lower than 1,00x10^{-3} SI Units, 1,00x10^{-3} SI Units to 3,00x10^{-3} SI Units, 3,00x10^{-3} SI Units to 6,00x10^{-3} SI Units and larger than 6,00x10^{-3} SI Units).

Asphalt samples were tested for the Indirect Tensile Strength (ITSR) and the 72 hours swelling test. Best results were produced from the last two groups which means MAG values of 3,00x10^{-3} SI Units to 6,00x10^{-3} SI Units and MAG values larger than 6,00x10^{-3} SI Units. The results can be viewed in table 28.

Table 28 : Results of asphalt experiments on different groups of samples (according to their MAG values)

	Magnetic susceptibility (x10^{-3} SI Units)	
	3 - 6	>6
Swelling 72 hours (%)	0,36	0,27
ITSR (%)	81,4	81,2

It is obvious from the results mentioned in table 28 that for asphalt applications, samples with MAG values greater than 3,00x10^{-3} SI Units have produced good results (this MAG threshold corresponds to LOI threshold of less than 3%). The outcome for swelling after 72 hours as well as the ITSR are both within acceptable range (as discussed with the head of asphalt laboratory and based on the state´s standards and regulation).

13.3 Results and discussions

The transferability of the new developed quality indices known as loss on ignition and magnetic susceptibility were successfully examined on the natural crushed rocks (as the primary materials for railway ballasts and asphalt) of the second quarry. The results of previous chapters were fully adapted to the second quarry and the same behavior and outcome was observed.

For the new quarry, which had an andesite/trachy-andesite rock type, the thresholds for magnetic susceptibility as well as the loss on ignition were defined and the transferability of magnetic susceptibility on field operations was verified. This threshold was defined for both cases: railway ballast and asphalt.

In case raw-materials are used as railway ballasts, on the basis of the reference experiments and more than 7000 LOI and MAG measurements, the threshold for loss on ignition was defined to be about 3,5% (for powders smaller than 1mm in size) and respectively the threshold for magnetic susceptibility was determined to be $1{,}00\text{x}10^{-3}$ SI Units on the drill cuttings. Based on the measurements performed on the whole quarry, the probability graphs for MAG and LOI values were plotted (figures 146 and 147). From both figures, it is clear that taking either of the MAG or LOI thresholds, about 50% of the quarry lies under the threshold value and about 50% of it lies over it. This means that based on the quality thresholds, almost 50% of the crushed rock produced from this quarry are qualified to be used for railway ballast and the other 50% (with low quality) may be used for other applications such as concrete production.

For asphalt usages, according to the results of different experiments, the MAG threshold was preferably higher and chose to be $3{,}00\text{x}10^{-3}$ SI Units and the threshold for LOI was under 3%. Accounting the mentioned limits for asphalt applications, almost 35% of aggregates from the quarry are qualified (figures 146 and 147).

Among the two quality indices, the magnetic susceptibility is chosen as the major parameter for predicting the quality of aggregates. The selection of MAG as the principle quality factor is due to some of its clear advantages such as time saving, being user-friendly, grouping of the measurements in larger ranges and reproducibility of its results.

With regard to this issue and according to the MAG measurements taken on the wall of the quarry with their corresponding X and Y co-ordinates, the three dimensional model of the quarry was produced.

As illustrated in figure 150, the threshold of the MAG value (as the main quality index) was set to $1{,}00 \times 10^{-3}$ SI Units for the railway ballast materials. The areas colored with green are regions with qualified quality (MAG value higher than $1{,}00 \times 10^{-3}$ SI Units) which accounts for about 50% of the whole quarry. The magenta color which shows the other 50% of the quarry are the low quality materials (MAG values lower than $1{,}00 \times 10^{-3}$ SI Units).

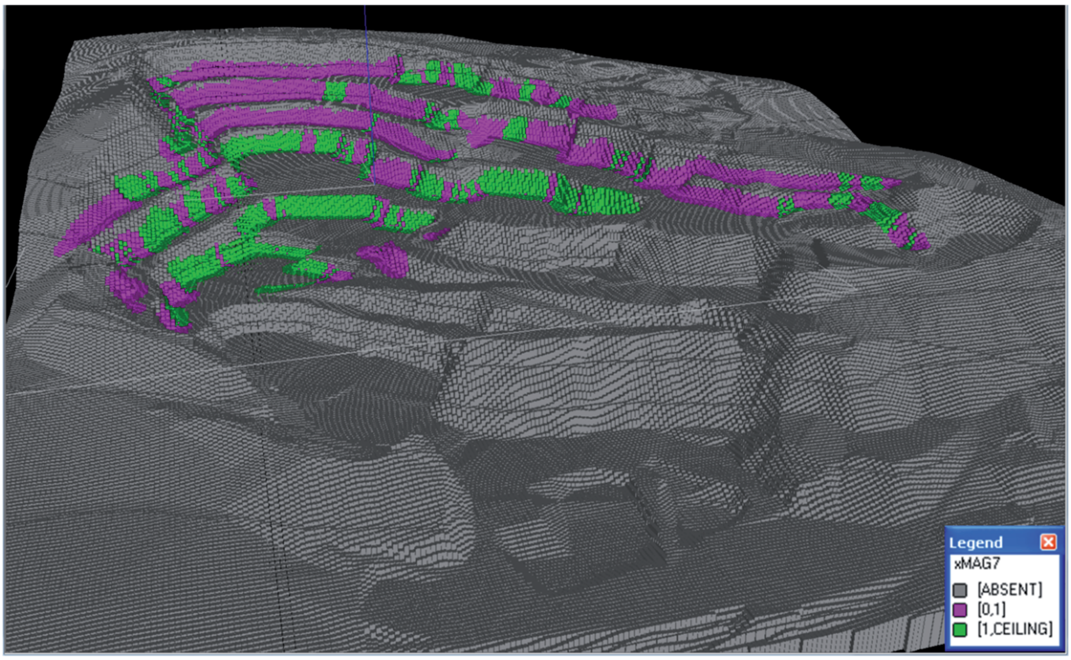


Figure 150 : Three dimensional model of the quarry on the basis of magnetic susceptibility threshold of $1{,}00 \times 10^{-3}$ SI Units. On this basis, about 50% of the hard rocks in the quarry are useful for railway ballast applications

14 Results and discussions

The civil construction industry has been encountering two relatively old problems namely natural crushed rock disintegration (without any initial clue of break down) with the passage of time and asphalt stripping issue. Distinguishing, controlling, or even avoiding the aforementioned problems from (or prior to) happening was the main objective of this research study which is presented under a PhD framework. Thousands of measurements and experiments were performed to understand these problems and find the right factors and parameters for their early recognition, in order to take the right preventive action. The major target of this study was not only to develop a method for the recognition of this obstacle confronted by the civil industry but also to find the so-called on-line process, which leads to the early recognition of the quality of raw-materials/asphalt prior to their production.

Many researches and studies has been performed on this issue and as a result many indices and processes have been developed for recognizing this complicated problem, but a real, universal, quick, reproducible, economic, trustable, representative, realizable and practicable on the field-site has never been developed. The lack of such a method has brought many troubles and exerted much pressure in the form of claims on the related construction industries. These obstacles have never been really solved and the corresponding industries have paid a lot as compensations. It has been a dream to be able to estimate the durability of the natural crushed rocks and consequently their quality prior to their mining and exploitation. It holds true also for the asphalt industry where the problem of stripping has long been the major enemy of asphalt quality. Presentation of a novel method, which helps in recognizing the quality of asphalt prior to its installation and construction process, is vital for asphalt industry. The currently progressed indices that were developed under extensive laboratory and field measurements are named as loss on ignition and magnetic susceptibility. These two indices have been approved to be great indices for estimating the aggregates quality utilized in railway ballasts and asphalt industry.

To be sure about the compatibility, effectiveness, and productivity of this inventive practical concept, the aforementioned techniques were justified and verified not only on one quarry but also on three different igneous hard rock quarries that two of which were mentioned in this thesis.

In this phase, which is the final part of this research work, based on the executed laboratory experiments and field tests in the quarry and in the asphalt plant, the major obtained results for both cases will be briefly reviewed.

14.1 Railway ballast

The primary approach started with the first quarry. Reconnaissance studies (consisting of geological, microscopic and geo-chemical multi-elemental analysis) on the samples from the quarry revealed that samples with lower quality have undergone a hydrothermal alteration process. A more detailed investigations on more number of samples showed that samples, which experienced the alteration, had higher value of loss on ignition. The thin/polished sections of these samples presented the hematization process where the magnetite minerals were oxidized thus altered to hematite under the influence of hydrothermal aqueous solution. In other word, samples with lower quality had higher value of loss on ignition and higher amount of hematite minerals or less amount of magnetite minerals. The amount of loss on ignition of a sample can be measured by a muffle oven (in weight percentage) and to evaluate the amount of magnetite mineral in a sample the magnetic susceptibility of the sample is measured. Magnetic susceptibility is measured by means of a portable hand-device magnetic susceptibility meter (measured in $x10^{-3}$ SI Units). As a result of the primary studies, the two factors namely loss on ignition (LOI) and magnetic susceptibility (MAG) had the potential of being used as quality indices. These two factors show an inverse relationship between one and the other, which means the increase of one led to decrease of the other one.

To be able to define a primary threshold for the MAG and LOI values, the “glycol test” was applied as reference test. According to the studies samples with MAG value of higher than $3{,}00x10^{-3}$ SI Units and LOI of lower than 2% showed a relatively acceptable durability and a satisfactory quality from themselves. $3{,}00x10^{-3}$ SI Units and 2% were primarily chosen as the limit for MAG and LOI values respectively which means samples with less than $3{,}00x10^{-3}$ SI Units of MAG value or higher than 2% of LOI, had low quality and vice-versa. As a result, the good quality samples must have a MAG value greater than the threshold and LOI value less than the defined limit.

Further laboratory measurements on a huge number of samples as well as thousands of field measurements (on the working faces of the quarry), not only approved the predefined thresholds, but also confirmed the above-mentioned fact more clearly: samples with low quality have high LOI/low MAG values and vice-versa. Based on the field measurements of the MAG and LOI values, three-dimensional models of the quarry were produced, presenting different zones of the quarry based on their MAG and LOI values thus depicting various qualities in the quarry. The 3-D model of LOI and MAG had a perfect correlation with each other, which means that either they both recognized a region as high quality material or as bad quality material.

The reproducibility of the results was justified by means of borehole drilling in different locations of the quarry. The drill cuttings of the boreholes were examined for their MAG/LOI values and then compared with the field measurements carried out on the walls of the quarry at the same location as the drilling boreholes. The values matched significantly with each other and the boreholes entirely confirmed the 3-D models.

With high degree of certainty about the behavior of the factors and their respective thresholds, it was decided to take the magnetic susceptibility as the major quality indicator. The reason for this choice was that it was quicker, more precise, and easier to perform. Of course, a conservative suggestion was to measure both indices. However, since time and easiness played an important role, the MAG value was selected as the main factor. Nevertheless in some special cases (such as the existence of other types of anomalies, sudden change of anomaly and overall change in physical appearance of the rocks) the LOI value was proposed to be controlled as well. The threshold for MAG value was set to be $3{,}00 \times 10^{-4}$ SI Units in the initial studies. However, in order to be able to separate low quality from high quality aggregates in a more precise manner and to be sure that the threshold led to a higher degree of accuracy, the MAG threshold value was determined to be $4{,}00 \times 10^{-3}$ SI Units. The MAG threshold value of $4{,}00 \times 10^{-3}$ SI Units resulted in a lower limit value for LOI as well (the new threshold for LOI was set to be lower than 2%).

Subsequently after determining the exact threshold of MAG value, the next stage was to check the transferability of the results of the MAG values from laboratory scale to the field scale. The main idea was to be able to implement this method directly on the drilling fines. For this purpose (transferring the laboratory threshold value to the field), more than 300 new boreholes were drilled. This phase was also performed with complete success and the MAG threshold value was correlated from the laboratory to the operational and industrial scale. The laboratory MAG threshold value of $4{,}00 \times 10^{-3}$ SI Units was transferred to the field drilling fines and returned a new MAG threshold value of 4,70x10^{-3} SI Units. On the basis of the results of this phase, the MAG threshold value was approved to be 4,7x10^{-3} SI Units for drill cuttings produced from the borehole drilling operation. Therefore, drilling fines with MAG values higher than threshold value were grouped as high quality materials and under this value as low quality materials.

The measurements of MAG values right on the drill cuttings during the drilling operation had many advantages. With this method, the quarry manager could be informed about the quality of the materials prior to blasting operation thus has the possibility to decide about the application of materials and their sales. This method is an “on-line” method for the recognition of the quality of the materials and is extremely quick, fast, reliable, and reproducible. Apart from a magnetic susceptibility portable hand-device, this method does not need any other special equipment or facilities. An important advantage of this technique is its representativeness. All of the previous methods needed hand-piece samples, which had to be prepared for experiments. The hand piece samples could only be gathered after the blasting operation and not prior to the blasting. On the other hand, out of hundreds of tons of blasted muck-pile only a few hand-piece samples were gathered which could not be representative at all. However, with this method the sampling is done on the borehole drill cuttings which itself is a representative mixture of about 20 meters of materials underneath it (the height of each drilling borehole in a quarry is about 15-20m). In other words, hand-piece samples present the rock properties whereas drill cuttings show the rock mass specifications. For each blasting operation, tens of these boreholes are drilled and a representative sample of each borehole is collected right on the borehole location and immediately tested for its MAG value. Therefore, this method is to a large extent representative for the whole muck-pile and delivers the results before blasting operation. Thus, after blasting, the quarry manager knows what has to be done with the muck-pile and it will be sold to the right customer based on its quality.

The selected MAG threshold value for the drill cuttings was also approved through a pure statistical quality control (SQC) method known as “fractal modeling.” Based on this method the probability graph of the MAG measurements was plotted and the inflection point of this graph was taken as the separation point of the MAG populations, meaning that different populations were integrated in the measurements. This method resulted in the creation of two distinct populations namely a high quality population and a low quality population. The separation point corresponded exactly to the determined threshold which was 4,70x10^{-3} SI Units. By the use of this method it was also confirmed that samples which had a MAG value of less than 4,70x10^{-3} SI Units had a low quality and samples with higher MAG values of 4,70x10^{-3} SI Units had a high quality. Therefore, the selection of the threshold as 4,70x10^{-3} SI Units was verified to be right. Based on this threshold, the three dimensional model of the quarry upon the latest measurements was also created.

For the second quarry, which had a different rock type from the first quarry, the same systematic operations were adopted. The selection of loss on ignition and magnetic susceptibility as two indicators for recognizing the quality of aggregates was also approved in the second quarry. The inverse relationship between the LOI and MAG values also held true in this quarry. On the basis of different laboratory and field experiments, the laboratory thresholds for MAG and LOI values were determined to be 1,00x10^{-3} SI Units and around 3,5% respectively. Exactly the same as the first quarry, the magnetic susceptibility was chosen as the main quality indicator although the measurement of LOI was also suggested in some special cases (such as change in anomaly or in case of doubts about the MAG behavior based on the physical appearance of the rocks). The reproducibility and transferability of the MAG results were approved on the field scale again. According to the field experiments the threshold for MAG value was set to be 1,00x10^{-3} SI Units on the drilling fines of the boreholes. Therefore, samples (drill cuttings) with MAG values lower than 1,00x10^{-3} SI Units had a poor quality and drill cuttings with MAG values higher than 1,00x10^{-3} SI Units had high quality.

The determination of the magnetic susceptibility and loss on ignition as the quality indices and their corresponding thresholds is based on detailed studies of the rock type of the quarry (which means exact assessment of physical and chemical characteristics of the rock type). These indicators are unique for each igneous hard rock quarry and the thresholds cannot be simply transferred from one quarry to the other. Detailed investigations are required for each quarry in order to verify and justify the right threshold value for it. Therefore, just to emphasize again, neither the threshold for magnetic susceptibility nor the threshold for loss on ignition are transferable from one quarry to the other. Their determination for each hard rock quarry, demands detailed/deepened inquiries and it is a function of geology, rock type physicochemical characteristics and rock formation processes.

14.2 Asphalt

The same as the railway ballast studies, the primary phase of investigations on asphalt quality initiated with the study of the raw materials from the first quarry, which were utilized as asphalt aggregates in the Hot Mix Asphalt production plant. As discussed in detail in the previous chapters of this research work, the affinity problem of asphalt, which is the loss of adhesion force between bitumen and aggregate, is one of the major problems in asphalt industry (regarding the asphalt quality issue). This obstacle is known as “stripping” in the asphalt industry and water is recognized as the main reason and principal component of this phenomenon. Stripping has long been the main concern of the asphalt producers and its related manufacturers. Many researches and studies have been carried out on this issue resulting in the origination of many theories and mechanisms.

The estimation and evaluation of the asphalt quality was acquired through three different stages:

i. The presentation of a new theory and the relationship between the developed quality indices (for early recognition of igneous hard rock quality) and the new theory
ii. The influence of the quality indicators (LOI and MAG) as well as thermal processes on the quality of asphalt
iii. Final complementary investigations

Regarding the asphalt stripping issue a new theory, namely “water discharge” theory was presented and approved via various types of experiments. This theory states that the existence of water (in different forms such as pore-water, gel water, crystal water, and moisture) in an aggregate particle leads to the disruption of bitumen film from the aggregate surface because of the generated water vapor pressure under high temperature gradients. The mechanism and extent of this rupture is a function of aggregate water content, porosity, alteration degree, and mineralogy. As the aggregate passes through the dryer drum, it is heated thus its water content gets out in form of water vapor. When the aggregate is mixed with bitumen, since it is still hot and its total water content is not completely evaporated, the remaining water vapor exerts pressure on the bitumen layer resulting in the formation of craters, vents, pits and air bubbles in the bitumen layer and underneath the bitumen film. The craters have the potential of playing as an inlet for water attacking from outside (e.g. rainwater) and the air bubbles will burst (under traffic load) and create a hollow space for further water aggregation.

On the other hand, a part of the aggregate water vapor that could not escape out from the bitumen layer, gathers underneath the bitumen film and condensate, leading to the creation of water-film at the interface of bitumen and aggregate surface. In both cases, the water vapor pressure results in loss of adhesion and causes stripping of bitumen from the aggregate surface. On the other hand, it can also cause loss in cohesion force. The existence of craters and vents in the bitumen layer around the aggregate surfaces, leads to the lack of adequate cohesion force between the aggregate grains themselves. The craters and pits cause lack of full contact between the neighboring aggregates. Therefore, the inadequate cohesion force among the adjacent aggregate grains, results in deficiencies in the asphalt mastics. Other factors such as time, traffic loads, weather, and environmental conditions also have negative effects on this issue and could worsen this phenomenon.

This theory was approved by means of different types of analysis. Experimental investigations such as loss on ignition, pressure tests, microscopic experiments, X-ray tomography, and SEM all confirmed (the accuracy of) this theory. The direct effect of the defined quality indices (namely MAG and LOI of the aggregates) on water discharge theory, were also tested and validated. As a result of this stage of experiments, no matter what kind of material was used as aggregate type, the water discharge theory held true for any kind of aggregates (before and after mixing with bitumen). Furthermore, (in regard to the aforementioned theory) it shall be emphasized that the low quality aggregates had more negative effects than the high quality aggregates. The low quality aggregates (aggregates with low MAG values and high LOI values) showed a more water content amount from themselves (as expected). Therefore, more water emission was generated in form of vapor, which resulted in the production of higher water vapor pressures, and thus the formation of higher number of craters, vents, pits, and air bubbles. As a result, the stripping of asphalt from low quality aggregates did happen faster and easier compared to high quality aggregates.

In the second phase of asphalt quality investigations, the direct effect of LOI and MAG values on asphalt quality was examined. The effect of thermal processes in a HMA plant on asphalt quality and correspondingly on stripping problem, was studied in detail as well.

The aggregates used for asphalt samples were categorized on the basis of their MAG values (as mentioned in previous sections, the threshold for MAG value was set to be $4{,}70\times10^{-3}$ SI Units). The high quality aggregates group had a high MAG values and low

LOI amounts, and the low quality aggregates had low MAG and high LOI values. Different asphalt samples were produced and examined (based on DIN Standards, TP-Asphalts and other regional requirements) for their Marshall swelling, Marshall stability loss, 72 hours swelling and ITSR. All various types of experiments confirmed the effect of MAG/LOI values of the aggregates on the quality of asphalt samples. The higher the MAG value, the lower the Marshall swelling and Marshall stability loss and vice-versa. The application of aggregates with high MAG values (higher than the threshold value) for the production of HMA was strongly recommended.

To evaluate the effect of thermal processes on the quality of asphalt, the different sections of HMA production plant with concentration on temperatures and retention times were studied. Various asphalt samples were produced with special methods to model the processes in the asphalt plants. Based on our observations and analysis, heating up the aggregates to very high temperatures in dryer drums and long retention times in any part of the asphalt plant, results in the decrease of asphalt quality. To be more precise, high retention times in silos and over-heating the aggregates in the dryer drums leads to high swelling and high loss of stability, thus decreasing the asphalt quality.

As a result of the second stage of asphalt studies, the consideration of the following remarks are of significant importance:

i. The aggregates must not be overheated (not more than 200°C) which means the HMA production plant must not operate under high temperatures (such as mixing the overheated aggregates with a temperature of 280-320°C with cold/warm recycled asphalt). The direct effect of this issue is that when the aggregates are over-heated, they are over-dried, and this phenomenon leads to larger swelling percentages and higher stability losses.
ii. Overheating the aggregates enhances the wettability characteristics of the aggregate surfaces. It means by rising the temperature, the contact angle decreases and therefore the aggregate surface shows more water affinity from itself (as mentioned in chapter 3 of this thesis).
iii. Short heating durations or respectively short retention times in the dryer drum is recommended since it avoids over heating of the materials.
iv. Avoiding long storage time intervals in the storage silos after the heating stage (dryer drum). Storage silos may refer to hot aggregate storage

silos or storage silos of final asphalt product. High retention time in these silos causes over-drying of aggregates, thus more water vapor emissions and therefore faster stripping of bitumen from the aggregate surface in next stages.

v. Transferring the final asphalt product to the installation/construction site as quick as possible so the retention time of asphalt in hot thermal condition is reduced.

vi. Avoiding long transport distances

The confrontation of the quarry with a new anomaly, directed the investigations to a third stage or namely complementary studies. The mining operation was advancing through a new region where the rock samples showed high MAG and LOI values simultaneously. Geological, microscopical, and geo-chemical studies showed that another type of hydrothermal alteration (known as serpentinization and chlorotization) affected the new encountered location where the magnetic content of the rocks remained more or less constant and the volatile content of the rocks increased significantly. Therefore, the samples from this area revealed a high magnetic susceptibility values as well as high loss on ignition values.

Based on the recognition of the new anomaly, complementary asphalt experiments were designed in order to determine a LOI threshold value as well (for asphalt quality applications). According to the new studies, the limit for loss on ignition was defined to be 0,75%. On this basis, aggregates recognized as high quality rocks for asphalt usages must have a MAG value of higher than 4,70x10^{-3} SI Units and a LOI value of less than 0,75%. Aggregates, which do not satisfy the mentioned threshold, shall not be used for asphalt applications.

The application of MAG and LOI as asphalt quality indices were also verified in the second quarry, which had another igneous rock type. Sampling from the second quarry was done and asphalt samples were produced based on the defined MAG and LOI thresholds (MAG threshold was 3,00x10^{-3} SI Units and LOI threshold was under 3%). The positive effect of MAG and LOI values on the quality of asphalt samples was fully confirmed, which means asphalt samples with high MAG values and low LOI values, showed low swellings/loss of stabilities.

In conclusion, I have to mention that our industry partner has used our proposed igneous-hard-rock/asphalt quality indices since the year 2010 and until now, no quality problem was reported on behalf of their customers and they are fully satisfied with this innovative on line method.

We strongly recommend that the use of selective mining method on the basis of LOI and MAG values must remain the dominant quarrying approach at the studied quarries in the future.

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